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HYDROCARBONS IN POLLUTED AIR. COORDINATING RESEARCH COUNCIL. SUMMARY REPORT

Edgar R. Stephens

California University

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Two main objectives of the study were to compare the distribution of hydrocarbons in the atmosphere with those observed in sources and to estimate the degree to which hydrocarbons of different reactivity participate in the photoreaction. Typical photochemical smog hydrocarbons can be described as auto exhaust plus gasoline vapors plus natural gas. Samples taken near specific sources (petrochemical plants, brush fires, oil fields) show distinctly different distributions. Afternoon smog samples show substantial attenuation of the more reactive hydrocarbons (specifically the olefins). By study the relative amounts of acetylene, ethene and propene it was possible to estimate the extent and time of reaction. Irradiation produces continued reaction for 24 hours or more. In six to eight hours of irradiation even hydrocarbons of low reactivity participate in the reaction; after the first hour or so the olefins of high reactivity are gone and further reaction depends on hydrocarbons of medium and low reactivity present in much larger quantity.

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SUMMARY REPORT
JUNE 1973

HYDROCARBONS IN POLLUTED AIR

COORDINATING RESEARCH COUNCIL
PROJECT CAPA-5-68

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Forward:

This project was begun in July 1968 as a continuation of earlier studies on ambient air hydrocarbons supported by a grant from the American Petroleum Institute. Some of the work has been reported in the published literature (see reference list). The data presented in these papers is summarized but not reported in detail in this report. The following were members of the project advisory committee: R. G. Larsen, H. E. Alquist, P. R. Ryason, C. S. Tuesday, A. P. Altshuller, J. C. Neerman and J. M. Heuss.

Acknowledgment

Mr. Frank Burleson did the bulk of the laboratory work reported here. Long path infrared studies were carried out by Mr. Monty Price and Mr. William Snider. Mrs. Minn Poe developed the computer program. We are also indebted to those persons who collected samples in distant locations.

Summary & Conclusions

Flame ionization chromatography provides a satisfactory procedure for analysis of hydrocarbons in polluted air. By freezing out the hydrocarbons present in a 100 ml sample of polluted air, concentrations as low as 0.1-0.2 ppb can be detected. With careful calibration and attention to detail, accuracy and precision of a few percent can be attained at levels of a few tens of ppb. Three instruments, with three different columns, were used to analyze about three dozen hydrocarbons. The small sample requirement permitted shipment of samples from many locations around the country and some from overseas.

The two main objectives of the study were to compare the distribution of hydrocarbons in the atmosphere with those observed in sources and to estimate the degree to which hydrocarbons of different reactivity participate in the photoreaction. Typical photochemical smog hydrocarbons can be described as auto exhaust plus gasoline vapors plus natural gas (in addition to background methane of 1.39 ppm). Spilled gasoline, as opposed to vaporized gasoline, does not seem to play a significant role. Samples taken near specific sources (petrochemical plants, brush fires, oil fields) show distinctly different distributions. Afternoon smog samples show substantial attenuation of the more reactive hydrocarbons (specifically the olefins). By studying the relative amounts of acetylene, ethene and propene it was possible to estimate the extent and time of reaction. It was concluded that oxidant smog as seen in Riverside has undergone six to eight hours of photochemical reaction. Irradiation produces continued reaction for 24 hours or more. In six to eight hours of irradiation even hydrocarbons of low reactivity participate in the reaction; after the first hour or so the olefins of high reactivity are gone and further reaction depends on hydrocarbons of medium and low reactivity present in much larger quantity. The practical conclusion is that reduction in the already low concentrations of the highly reactive olefins will not have much practical effect.

During the course of this research program, reports came out which indicated that the higher aromatics (C_8^+) were much more reactive than previously thought. Irradiation of ambient air mixtures confirmed the

moderate reactivity of these compounds. Meanwhile it was reported that benzilic hydrocarbons could be oxidized under atmospheric conditions to the potent eye irritant peroxybenzoyl nitrate. This suggested that one active species attacks the aromatic side chain while some different species attacks the ring. Tests were made to see if the side chain attack could be due to nitrogen trioxide. High concentration experiments in a long path cell indicated that this could be so but yields were small and rates were slow. No reaction could be detected at realistic (ppb) concentrations.

PROCEDURES & ANALYSIS

Three gas chromatographs are used with four procedures to quantitate about three dozen individual hydrocarbons in ambient air samples. Three of the four procedures require a freeze out of the hydrocarbons from a 100 milliliter air sample. The fourth procedure uses a 3 milliliter loop sample to analyze methane. Figure 1 illustrates the freeze out procedure. Samples are injected with a 100 milliliter glass medical syringe into a gas sample valve on which the normal sample loop is replaced by a freeze trap packed with chromatographic packing. No attempt is made to remove either water or carbon dioxide from the sample prior to freeze out. A bubble meter or syringe on the output side of the gas sample valve can be used to verify the fact that all the sample has, indeed, passed through the trap. Liquid oxygen is used to chill the packed freeze trap since it has a temperature sufficiently low to collect even such hydrocarbon gases as ethane, ethylene and acetylene, but not low enough to collect significant quantities of oxygen. If liquid nitrogen were used as the coolant oxygen would be collected from the

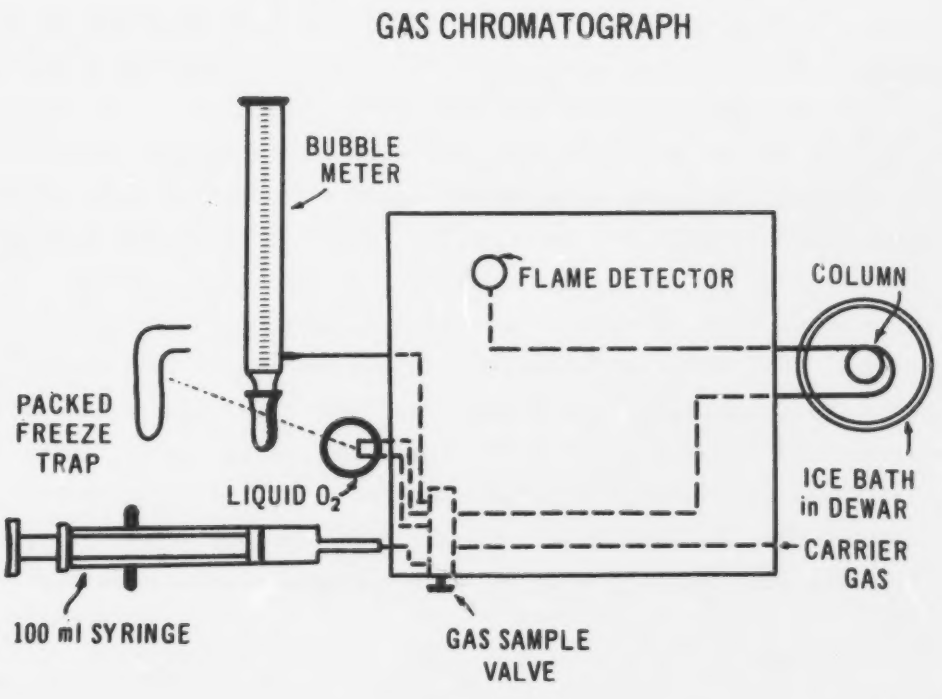

FIGURE 1

air sample and injected into the column along with the hydrocarbons. This would snuff the flame. Liquid argon could be used since its boiling point is very close to that of liquid oxygen. A third alternative would be to chill with liquid nitrogen and then to purge the trap with nitrogen or with helium prior to thawing and injection into the column. Injection into the column is accomplished by thawing the trap and simultaneously pushing the gas sample valve. Samples are then carried quickly into one of the three columns. Instrument No. 1, with the freeze out procedure, gives C_3 through approximately C_6 hydrocarbons plus acetylene. Instrument No. 2, with the freeze out procedure, gives ethane, ethene and acetylene. To measure methane, the freeze trap on this instrument is replaced by a sample loop and a 3 milliliter sample directly injected. The third instrument gives principally aromatic hydrocarbons plus acetaldehyde, propionaldehyde, acetone and methyl ethyl ketone. Alpha and beta pinene also emerge from this column, but they are not well separated from the aromatic hydrocarbons. Table 2 summarizes the columns and chromatographic procedures.

Freeze Out Trap

Freeze out traps were prepared by packing 20 cm lengths of stainless (2.34 mm I.D. [1/8 inch OD]) steel tubing with a chromatographic substrate consisting of 10% dimethyl sulfolane on 42/60 mesh C-22 firebrick or with glass heads. Each tube was bent into a "U" shape and attached to the gas sample valve of a chromatograph in place of the sample loop. The sample inlet and outlet of each sample valve were equipped with toggle valves. Although these freeze out methods had been found to be highly efficient by other workers[1] it remained to be proved that the specific technique in present use was also quantitative. This was done by analyzing a synthetic mixture containing about 1 ppm of each of several hydrocarbons, first using a direct sample loop injection, then by diluting the same volume of the mixture to 100 ml and using the freeze trap. The area under each peak was measured and divided by the carbon number to obtain a sensitivity factor as shown in Table 1. Although these trap samples were consistently smaller than the corresponding peaks from the loop injection by about 15%, the fact that the area per carbon atom was independent of

hydrocarbon volatility suggests that this discrepancy results from inaccuracy in the measurement or delivery of volumes rather than a failure to capture all the hydrocarbon. Dead space in the valve and connecting tubes may account for this difference. In any event the freeze-out procedure was used for calibration and quite reproducible results were obtained, as can be seen by examining some replicates in Table 4.

Table 1 —Trapping Efficiency—Area per Carbon Atoms (S_i) for Loop Sample and Two Trapping Techniques

Compounds	Trap (pull) S_i	Trap (push) S_i	Loop S_i	$\frac{S_i \text{ (loop)}}{S_i \text{ (trap)}}$
Ethane	0.153	0.153	0.169	1.10
Ethene	0.142	0.143	0.164	1.14
Propane	0.145	0.146	0.169	1.16
Propene	0.131	0.132	0.158	1.19
Total	0.571	0.574	0.660	
Propane	0.113	0.111	0.115	1.02
Propene	0.109	0.104	0.134	1.23
n-butane	0.113	0.114	0.129	1.14
Acetylene	0.145	0.132	0.157	1.07
1-butene	0.115	0.107	0.133	1.16
trans-2-butene	0.114	0.106	0.129	1.13
cis-2-butene	0.115	0.106	0.131	1.14
1,3-butadiene	0.112	0.102	0.127	1.13
Methyl acetylene	0.109	0.101	0.122	1.12
cis-2-Pentene	0.125	0.109	0.153	1.22
Total	1.170	1.092	1.330	

Note: First 4 compounds separated on chromatograph No. 2; remainder on chromatograph No. 1.

Loop: 2.9 ml volume
Trap: 2.9 ml diluted to 100 ml N_2 and frozen in trap

TABLE 2. Columns and Chromatographic Conditions

NUMBER 1

Column: 11 meters by 2.34 mm I.D. (1/8 inch OD stainless tube) containing 10% dimethyl sulfolane on 42/60 mesh C-22 firebrick maintained at $0^{o}C$ plus 0.46 meters by 2.34 mm I.D. stainless tube containing 10% carbowax E-600 on 42/60 mesh C-22 firebrick at room temperature to minimize background due to column bleed. Background signal at full sensitivity was about 4.3 mv. Carrier gas: 22 ml/min of dry nitrogen. Flame detector: 24 ml/min hydrogen and 287 ml/min oxygen. Wilkens Model 600 chromatograph.

This column gave good separation of acetylene, C_3 and C_4 olefins and paraffins, C_5 paraffins, some of the C_5 olefins and C_6 paraffins, as well as 1,3-butadiene, methyl acetylene and cyclopentane. Figure 2

NUMBER 2

Column: 1.52 meters by 2.34 mm I.D. (1/8 inch O.D. stainless tube) containing activated alumina held at $60^{o}C$. Carrier gas: 40 ml/min nitrogen. Flame detector: 40 ml/min hydrogen and 287 ml/min oxygen. Wilkens Model 600 chromatograph. Background signal at full sensitivity was 4.3 mv. Retention times and therefore peak heights were variable depending (apparently) on the moisture content of the carrier gas. This was therefore replaced by the following:

Column: 1.52 meters by 2.34 mm I.D. (1/8 inch O.D.) filled with Poropak N (100/120 mesh), operated at $60^{o}C$ with a carrier flow of 80 ml/min of nitrogen and 60 ml/min of H_2 and 410 ml/min of O_2. This gave a good separation of ethane, ethene and acetylene in a two minute chromatogram. Methane is not frozen out by these procedures but could be determined by direct injection of an air sample using a three ml loop. Since the worldwide background level of methane is nearly 1.4 ppm there is no need for the high sensitivity provided by the freeze-out procedures. This does mean, however, that a third chromatogram is required. Air samples gave negative responses, apparently due to oxygen, just ahead of the methane peak. Comparison of calibrations in nitrogen and in air showed that this caused no interference with the methane measurement. Figure 3

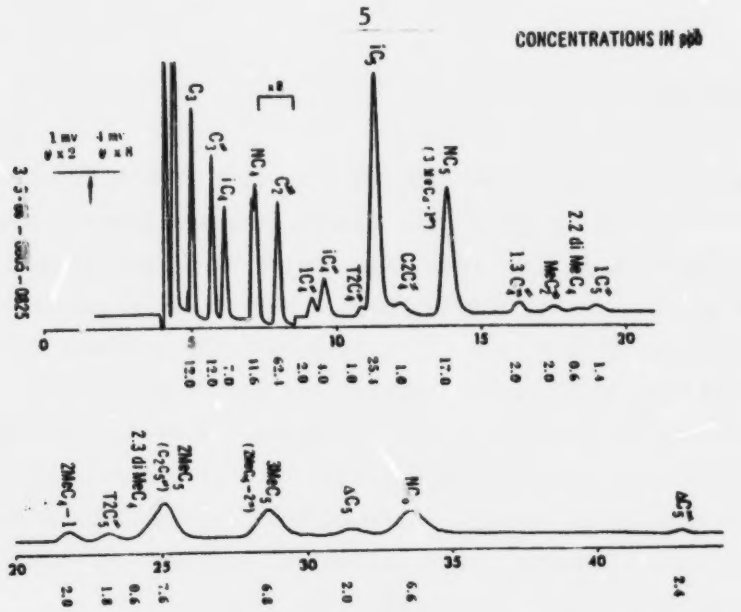

Fig. 2. Chromatogram of ambient air hydrocarbons on dimethyl sulfolane column.

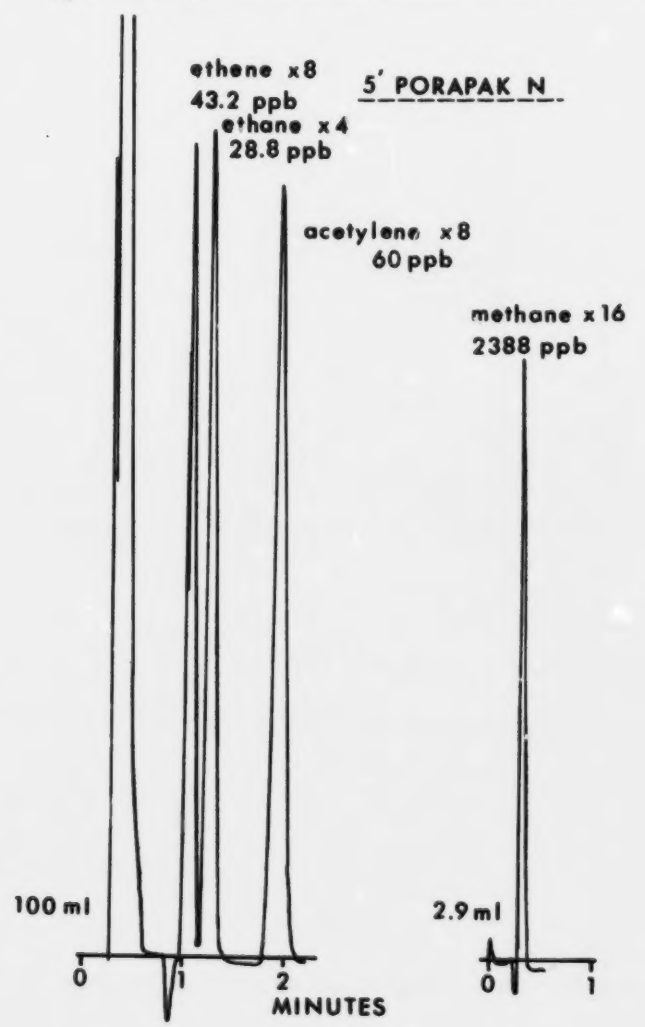

Fig. 3. Chromatogram of Ambient Hydrocarbons on Porapak

TABLE 2 (continued)

NUMBER 3

Column: 3.048 meters by 2.34 mm I.D. (1/8 inch O.D. stainless tube) filled with 5% of 1,2,3 tris (2-cyanoethoxy) propane plus 1.52 meters by 2.34 mm I.D. tube filled with 5% bentone34 and 5% dinonyl phthalate both on 100/120 mesh HMDS treated gas chrom W plus 0.915 meters by 2.34 mm I.D. filled with 10% carbowax E 600 on C-22 firebrick 30/60 mesh. Carrier gas was 38 ml N_2/min. Fuel flow: 25 ml H_2/min with 300 ml/min of oxygen. A freeze out trap containing uncoated glass beads was used with this instrument. It was used to measure aromatic hydrocarbons through C9. Alpha and beta pinene, acetaldehyde, propionaldehyde, acetone and methyl ethyl ketone could also be measured. See Figure 4.

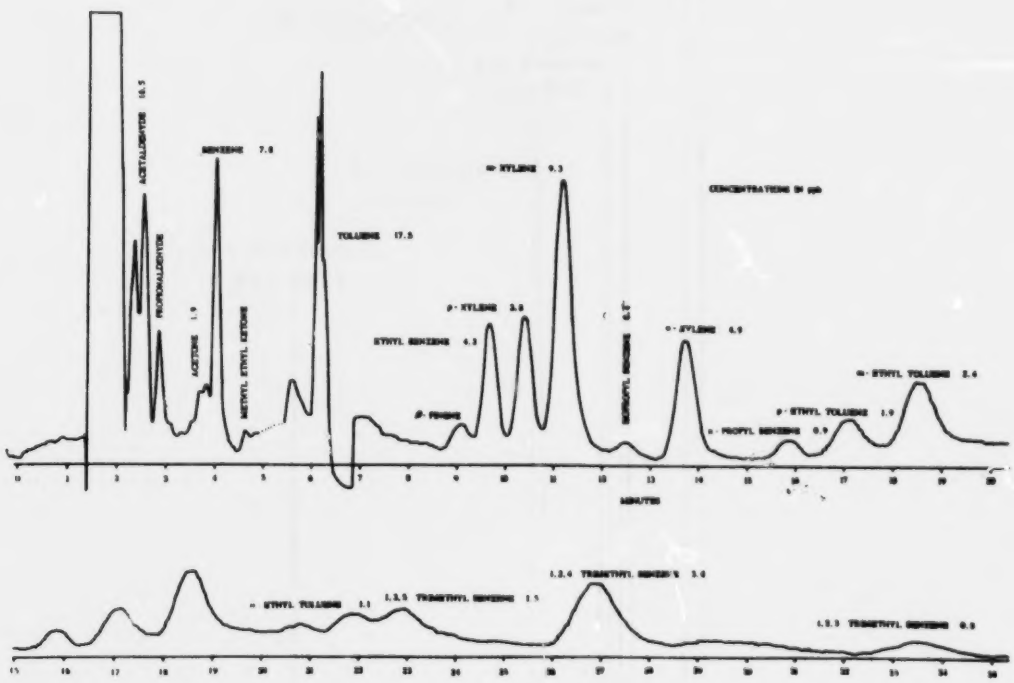

FIGURE 4

Ambient Air Chromatogram of Aromatics (Number 3)

Trapping efficiency was also verified by collecting a sample which had been passed through the freeze out trap in a second 100 millimeter syringe. This sample was then re-analyzed and found to contain only 0.2 ppb of ethane and ethene, although the input sample had contained 7.2 ppb and 8.0 ppb respectively of these hydrocarbons. The re-analyzed sample also contained fractional ppb concentrations of oxygenates.

Calibration

Emergence times are used to identify individual hydrocarbons on the chromatograms and peak heights are used to estimate concentrations which have always been reported in parts per billion by volume. A transparent overlay chart is used for rapid reading of peaks.

Calibration mixtures are prepared by successive dilutions of pure hydrocarbons into modified two liter Erlenmeyer flasks. These flasks have a stopcock attached to the drawn down neck, a three-way stopcock near the base and an injection port made from a ball and socket joint in the body of the flask.

Two such flasks are flushed with pure air or nitrogen. Two ml of each gaseous hydrocarbon is then added to the first flask from a small syringe. This gives about 1000 ppm in this flask. Liquid hydrocarbons are added from microliter pipettes. The amount is calculated from the handbook value of the density and the molecular weight. After mixing, two ml of this mixture is transferred to the second flask with a ground glass medical syringe. A number of hydrocarbons can be injected into the first flask at about 1000 ppm. A single transfer to a second flask then will yield a mixture of those hydrocarbons at 1 ppm. Although the flasks are open to the room air during the transfer of gases, there is no significant loss to the atmosphere if the flask's temperature and pressure are the same as that of the room. Five ml of this mixture diluted to 100 ml in a syringe then produces a calibration mixture containing about 50 ppb of each hydrocarbon. (The exact concentration will, of course, depend on the exact volumes of liquid and gas taken and the exact volumes of the dilution flask.)

TABLE 3
RIVERSIDE SMOG 1610 PST 10-24-68
(TWELVE SAMPLES, PPB)

Instrument 1			Instrument 2		
	$\bar{C}$	σ		$\bar{C}$	σ
PROPENE	1.27	0.1	METHANE	2530	30
PROPANE	49.9	2.2	----------		
ISOPENTANE	41.2	1.5	ETHANE	72.2	2.3
N-HEXANE	8.3	0.4	ETHENE	17.9	1.2
ACETYLENE	41.3	1.3	ACETYLENE	42.8	1.5

Precision

Table 3 shows the precision which can be attained with these methods. This table gives the average concentration ($\bar{C}$) and the standard deviation (σ) for a set of twelve ambient air samples of unusual uniformity.

At the highest concentrations, the relative standard deviation is just over 1% (CH_4). In the range of 10's of ppb, it is 3 to 5% while at the 1 ppb level it is near 10%. This of course also depends on the particular peak. For propane at 1.27 ppb, the standard deviation was 0.1 ppb. These standard deviation values reflect both the measurement precision and the variation between the twelve samples. If the acetylene values from the two instruments differ by more than about 10% at the 40 ppb level, a search is begun for some malfunction of one of the instruments. In Table 3 the acetylene values differ by only 1.5 ppb (about 4%).

Stability of hydrocarbon concentrations while stored in these sample tubes was verified by repeating analyses after one or more days of standing. Table 4 compares concentrations of hydrocarbon samples taken in 20 liter carboys. These two samples were taken on the second floor and on the roof of the Riverside County Health-Finance Building. The roof top sample was stored in the dark and showed no change after 24 hours. The second floor sample was nearly identical and was irradiated 24 hours with the results shown in Table 4.

Sensitivity

When operating properly, minimum detectable peaks for short emergence time compounds corresponds to 0.1-0.2 ppb (for 100 ml freeze out). Compounds with longer retention times have broader peaks and therefore the minimum detectable concentrations are a few tenths or one ppb. This decrease in sensitivity with emergence time would be more pronounced if concentration were expressed by weight. Larger samples could easily be used to attain higher sensitivities.

Table 4 —Ultraviolet Irradiation of Ambient Air Riverside County Building of Health and Finance, 3/3/66, 08:05–08:25 PST, Sky Clear, Wind 5–7 mph, N.W., 40–45°F, Moderately Heavy Haze (Smudge)

Compounds	Concentration in ppb									
	Roof Top Sample	45 min Dark	24 hr Dark	2nd Floor Sample	1 hr Irrad. uv	2 hr Irrad. uv	4 hr Irrad. uv	8 hr Irrad. uv	20 hr Irrad. uv	24 hr Irrad. uv
Ethane	36.0	36.0	37.6	37.6	37.6	36.0	37.6	36.0	35.2	35.2
Ethene	45.6	45.6	48.8	51.2	45.6	40.8	36.0	27.2	16.0	12.6
Propane	14.0	14.0	15.0	14.6	14.2	12.6	13.6	12.8	12.2	11.4
Propene	14.0	13.8	15.4	15.6	11.0	7.6	4.4	2.2	1.4	1.4
Propane	12.0	12.4	12.2	13.0	12.8	12.2	11.8	11.2	10.2	10.4
Propene	14.0	13.8	11.6	13.4	9.4	6.6	3.8	1.4	0.8	0.6
Isobutane	7.0	7.0	6.8	7.4	7.0	6.8	6.6	5.8	5.0	4.8
n-butane	41.6	41.6	41.6	44.8	43.2	40.8	39.2	33.1	28.0	27.2
Acetylene	62.4	62.4	61.6	69.6	69.6	65.6	64.8	60.0	56.8	56.8
1-butene	2.0	2.0	2.0	2.2	1.4	1.0	0.6	0.4	0.4	0.4
Isobutene	4.0	4.0	3.4	4.0	2.4	1.4	0.8	0.6	0.6	0.4
trans-2-butene	1.0	1.2	1.2	1.4	0.4	0.0	0.0	0.0	0.0	0.0
Isopentane	25.4	25.4	25.2	27.6	26.0	24.6	22.8	19.2	14.4	13.6
cis-2-butene	1.0	1.2	1.2	1.0	0.4	0.0	0.0	0.0	0.0	0.0
n-pentane[a]	17.9	17.0	16.8	18.6	17.4	16.2	15.4	12.4	9.4	8.8
1,3-butadiene	2.0	2.0	2.0	2.4	1.0	0.6	0.0	0.0	0.0	0.0
Methyl acetylene	2.0	2.0	2.0	2.0	2.0	1.8	2.0	1.4	1.4	1.2
2,2-dimethyl butane	0.6	0.6	0.6	0.6	0.4	0.4	0.4	0.2	0.2	0.4
1-pentene	1.4	1.2	1.4	1.0	0.8	0.8	0.4	0.0	0.0	0.0
2-methyl butene-1	2.0	2.4	2.0	2.0	0.8	0.4	0.0	0.0	0.0	0.0
trans-2-pentene	1.8	1.6	1.6	1.6	0.6	0.0	0.0	0.0	0.0	0.0
2,3-dimethyl butane	~0.6	~0.6	—	~1.2	~0.7	~0.9	~0.8	~0.6	~0.8	~1.0
2-methyl pentane[b]	7.6	7.6	7.4	8.4	7.6	7.4	6.6	5.7	4.0	3.6
3-methyl pentane[c]	6.8	7.4	6.8	8.0	4.8	4.2	3.6	3.4	2.2	2.2
Cyclopentane	2.0	2.4	1.8	1.4	1.8	2.0	1.6	1.4	0.8	1.0
n-hexane	6.6	6.4	6.6	7.2	6.6	5.8	5.6	4.6	3.0	3.4
Cyclopentene	2.4	2.2	2.2	2.4	1.4	1.0	0.4	0.6	0.4	0.6

Note: First 4 compounds separated on chromatograph No. 2; remainder on chromatograph No. 1.
[a] Contains 3-methyl butene-1.
[b] Contains *cis*-2-pentene.
[c] Contains 2-methyl butene-2.

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Sampling

In the first work not enough attention was paid to the influence of sampling. While it is possible to measure hydrocarbons in a 100 ml sample of air with good precision and accuracy (if not completeness) to be at all useful these data must be used to infer the composition of some larger air mass. The hazards involved in this inferential process are sometimes underestimated. They are especially important in analyzing light hydrocarbons in ambient air at ground level which is the most convenient sampling location. An ideal system would be one in which the entire air parcel of interest (this might be several cubic miles) could be homogenized before measurement. The next best ideas is to choose a sampling area removed from sources and to average a number of samples. The separate analyses can then be used to

estimate the homogeneity of the air parcel. On the other hand, fluctuations from sample to sample can also be useful. Hydrocarbons which come from a common source must fluctuate together in concentration, while those which derive from different sources will not normally correlate well with each other. This technique was used to identify natural gas in urban air (see later).

Standard sample tubes of 300 ml to 1 liter in volume were used to sample in remote locations. It was convenient to transport or ship a dozen such tubes in a box. These tubes were fitted with a stopcock at each end and were filled by flushing with a rubber suction squeeze bulb. The sample, therefore, did not pass through the squeeze bulb. Laboratory evacuation of the sample tubes was avoided because there was no way to verify vacuum maintenance during transport to a distant sampling site. To transfer a sample into the freeze trap, a 100 ml syringe was filled with pure nitrogen, attached to the sample tube, the stopcock opened, and the sample and nitrogen mixed by working the syringe plunger back and forth a number of times. Tests were made to ensure that no significant leakage occurred during this process. The volume of the sample tube was used to calculate the degree of dilution that occurs in this process. After closing the stopcock the sample syringe was then connected to the gas sample valve on the chromatograph and the contents forced through the chilled trap. This procedure could be repeated several times so actually several 100 ml samples could be taken from sample tubes as small as 300 ml. Of course, the dilution factor becomes larger and larger as more samples are taken and this limits the process. Quite reproducible results can be obtained even at the low concentrations of ambient polluted air.

Samples taken at temperatures and/or pressures different from those prevailing in the laboratory must be first brought to laboratory pressure (about 1200 feet above sea level) by adding measured amounts of pure nitrogen from a 100 ml syringe or by venting the tube. The empty syringe is then attached to one inlet of the gas sample valve on the chromatograph while the sample tube is attached to the other.

With the valve in the sample position, the contents of sample bulb and 3 ml sample loop are mixed. This sample is injected into the chromatograph to provide a methane measurement. If nitrogen was added to bring the tube to laboratory pressure, a correction is made for this dilution.

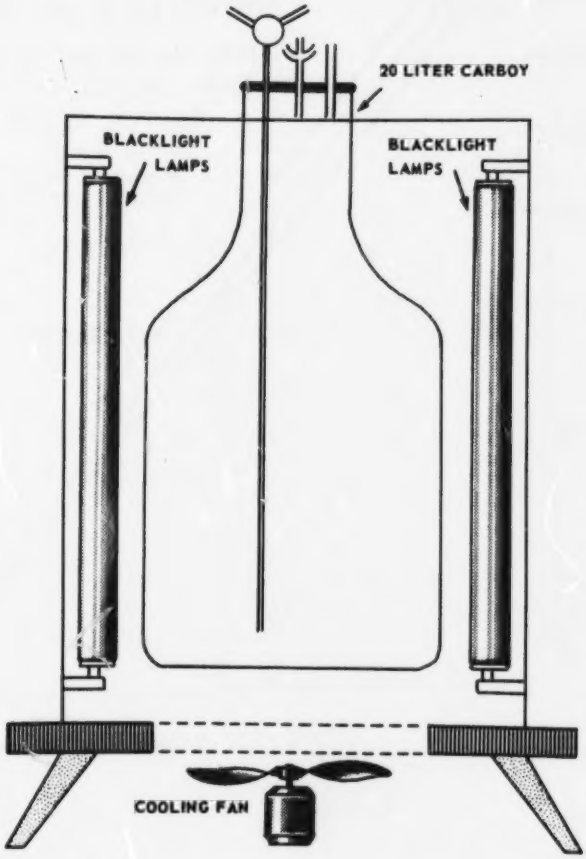
Larger samples of ambient air were taken in 20 liter (5 gal.) and 50 liter (12 gal.) borosilicate glass carboys. To provide an inert closure for these vessels, a special lid was devised. The mouth of the carboy was ground flat and a 1/4 inch thick glass disc containing epoxy cemented borosilicate glass inlet and outlet tubes was waxed on with fluorocarbon wax. One of the tubes extended to the bottom of the bottle, and the other into the top. In this way a suction pump could be used to purge the bottle and flush it with sample in a few minutes. A larger port, closed by a ball joint, was cemented in the lid and used for syringe or micropipet injection of standard samples. Samples in this bottle were in contact with glass almost exclusively with only minimum amounts of epoxy cement and fluorocarbon wax.

Irradiation

This bottle and an irradiation system which was used to irradiate ambient air samples is shown in Figure 5.

Twelve "blacklite" fluorescent lamps (15 watts each) were mounted in a framework as a vertical cylinder large enough to contain one of the bottles. A ventilation fan mounted below the bottle served to limit the temperature rise to 1 or 2°C. The light intensity in the center of the irradiation system was tested by photolyzing nitrogen dioxide at 0.5-5 mm Hg pressure in an ultraviolet absorption cell. Concentrations were then measured in a Cary Model 14 ultraviolet spectrophotometer. The half-life of nitrogen dioxide measured in this way was 1.3 min. These results are shown in Figure 6.

This half life is somewhat longer than that calculated and observed for outside sunlight on the brightest day (about 1 min.). This system was used to irradiate ambient air samples which were taken in early



BOTTLE PHOTOREACTOR

FIGURE 5

morning hours after a good purge of the atmosphere. Two such carboys were available so simultaneous samples could be taken and irradiated in natural sunlight and artificial light.

Stirred Flow

This system which originally employed 20 liter carboys and static irradiation techniques, was later elaborated to use a 50 l carboy and

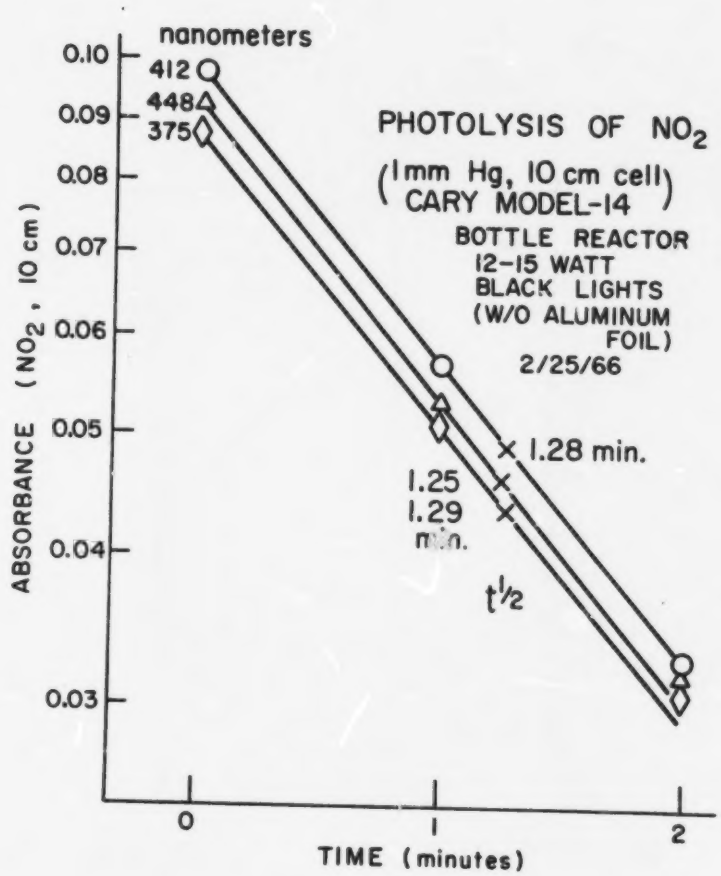
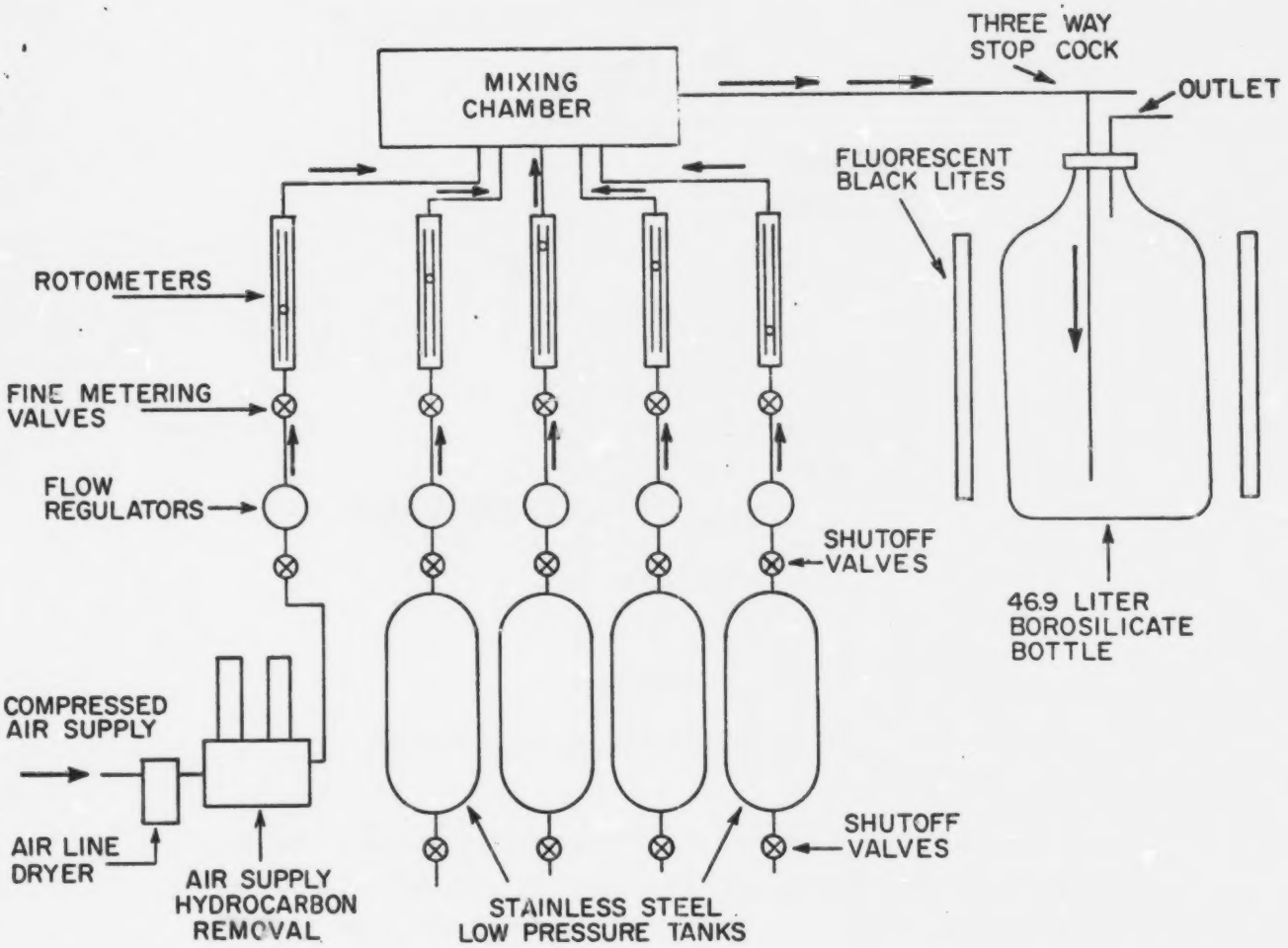


FIGURE 6

a stirred flow system. One borosilicate glass reaction vessel is mounted inside a set of 24-black light fluorescent lamps as irradiation source. These have been mounted on a cart along with supply tanks and flow and mixing equipment to supply the reactor. Included on the cart, in addition to the bottle photoreactor itself, are a heatless air dryer for air purification, supply tanks for the reactants, a flow mixing panel consisting of the flowmeters and suitable needle valves and space for analytical equipment (see Figure 7). The supply tanks are low pressure oxygen tanks, each of which is equipped with a pressure reduction regulator which feeds into a


THREE WAY
STOP COCK
MIXING
CHAMBER
OUTLET
FLUORESCENT
BLACK LITES
ROTOMETERS
FINE METERING
VALVES
FLOW
REGULATORS
SHUTOFF
VALVES
46.9 LITER
BOROSILICATE
BOTTLE
COMPRESSED
AIR SUPPLY
AIR LINE
DRYER
AIR SUPPLY
HYDROCARBON
REMOVAL
SHUTOFF
VALVES
STAINLESS STEEL
LOW PRESSURE TANKS

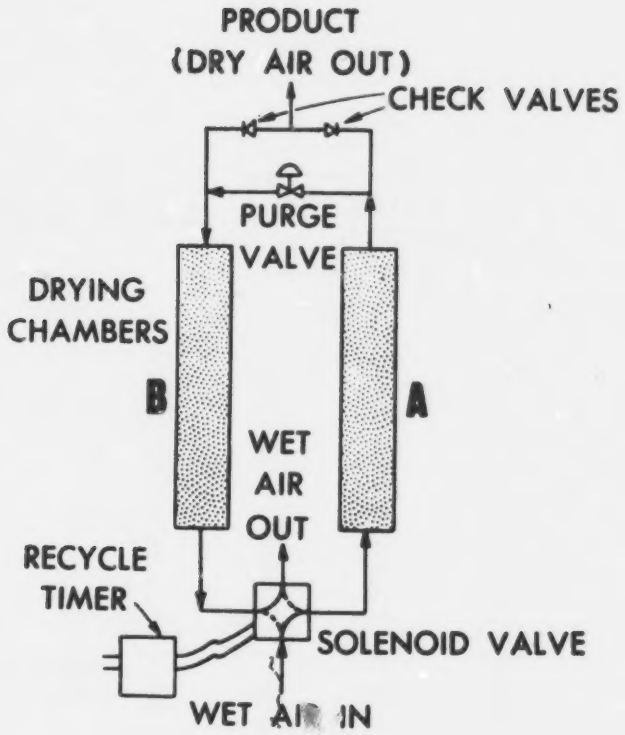


FIGURE 8

Heatless Adsorbtion Air Purification

manifold in a flow mixing panel. Needle valves are used for flow regulation. Four such tanks are mounted on the cart along with their valves and the flow panel. The heatless air dryer used for air purification is 3/4 filled with activated charcoal and 1/4 with the manufacturer's desiccant. This modification, as recommended by W. H. King of Esso Research, permits production of very pure hydrocarbon-free air. One column of the dryer adsorbs air pollutants in the charcoal while the other is being purged. It operates on a 30-second cycle and produces air with hydrocarbon concentration reduced to

the low ppb range. This is important since the ambient air in Riverside already contains concentrations in excess of those that we wish to study. The flow system has been designed to have a residence time variable from one-half to four hours. To accomplish this, a portion of the supply stream of dilute reactant can be diverted away from the bottle and used for an input analysis. This permits analysis of input and output streams simultaneously. Table 5 gives performance data on the air purifier.

TABLE 5

HYDROCARBON REMOVAL BY TWO COLUMN HEATLESS FRACTIONATOR

	CONCENTRATION ppb	
HYDROCARBON	Unfiltered Ambient Air	Filtered Air
METHANE	2,028	1,058
ETHENE	9.4	0.6
ETHANE	23.2	1.4
ACETYLENE	11.6, 11.2	1.2, 1.4
PROPANE	13.4	1.6
PROPENE	1.4	0.4
ISOBUTANE	4.8	0.1
n-BUTANE	13.4	0.2

This reactor was designed primarily to study the reactions of aromatics at the realistic concentration range. In such circumstances the question of loss of reactants by adsorption on the wall of the reactor is usually raised. This is especially important when compounds of low volatility are being studied. In a tube flow system used on an earlier project it was found that adsorptions of light hydrocarbons or even of PAN on clean reactor walls was not a significant factor. This type of experiment was repeated with toluene and acetylene in the new flow reactor. With 254 ppb of toluene in the bottle a steady flow of 0.86 liter/min of pure air was used to purge the bottle. Chromatographs #2 and #3 were used to monitor the acetylene and toluene concentrations with time. Multiplication of the reactor volume by the concentration of toluene gives the amount of toluene present initially in the gas phase (11,900 nl as a vapor, see Figure 9). Integration of the purging curve in this figure gives the amount of toluene removed from the reactor (11,280 nl in Figure 9). Since these two figures agree we conclude that little toluene was desorbed from the reactor surfaces during purging. It should be noted that this procedure does not require an absolute calibration of the chromatograph.

Data of this type can also be used to evaluate mixing in the reactor. Perfect mixing corresponds to exponential dilution and should follow the equation

$$\ln C/C_0 = -\frac{F}{V}t$$

Figure 10 shows a logarithmic plot of acetylene and toluene for this purge experiment. Both follow closely the theoretical curve for the volume and flow rate indicating adequate mixing.

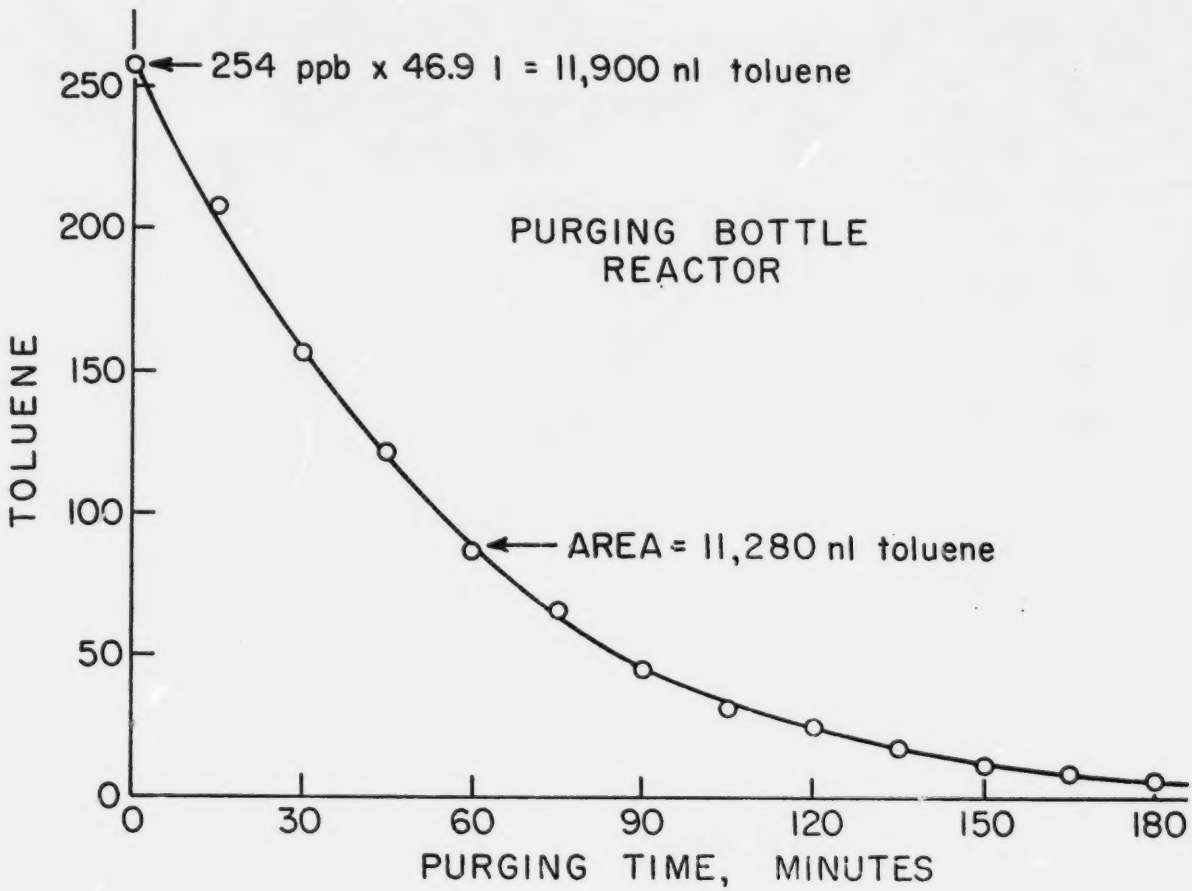

254 ppb x 46.9 l = 11,900 nl toluene
PURGING BOTTLE
REACTOR
AREA = 11,280 nl toluene
TOLUENE
250
200
150
100
50
0
0
30
60
90
120
150
180
PURGING TIME, MINUTES

FIGURE 9

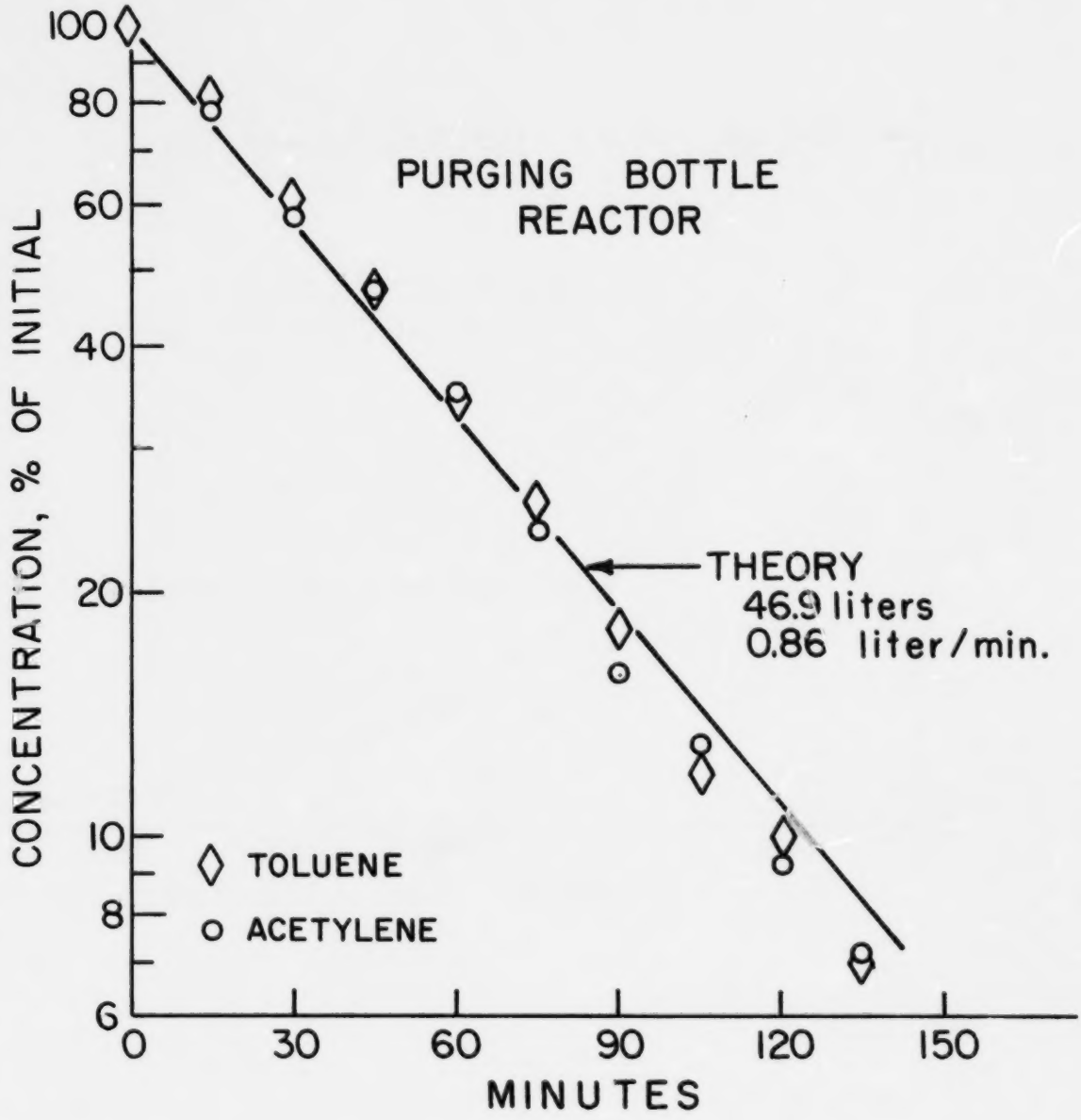

PURGING BOTTLE
REACTOR
THEORY
46.9 liters
0.86 liter/min.
TOLUENE
ACETYLENE
CONCENTRATION, % OF INITIAL
MINUTES
100
80
60
40
20
10
8
6
0
30
60
90
120
150

FIGURE 10

RESULTS IN AMBIENT AIR

Smog Hydrocarbons

The pattern of hydrocarbon concentrations as found in Riverside photochemical smog is quite consistent; changes in the relative amounts of hydrocarbons are much smaller than the changes in the concentrations from clean air to smog air. The analysis taken when a 0.6 ppm oxidant smog was recorded on 6 August 1970 (a record for that year in Riverside) is typical (see Figure 11). In this figure and others like it in this report, the hydrocarbons are plotted according to the listing in Table 6 .

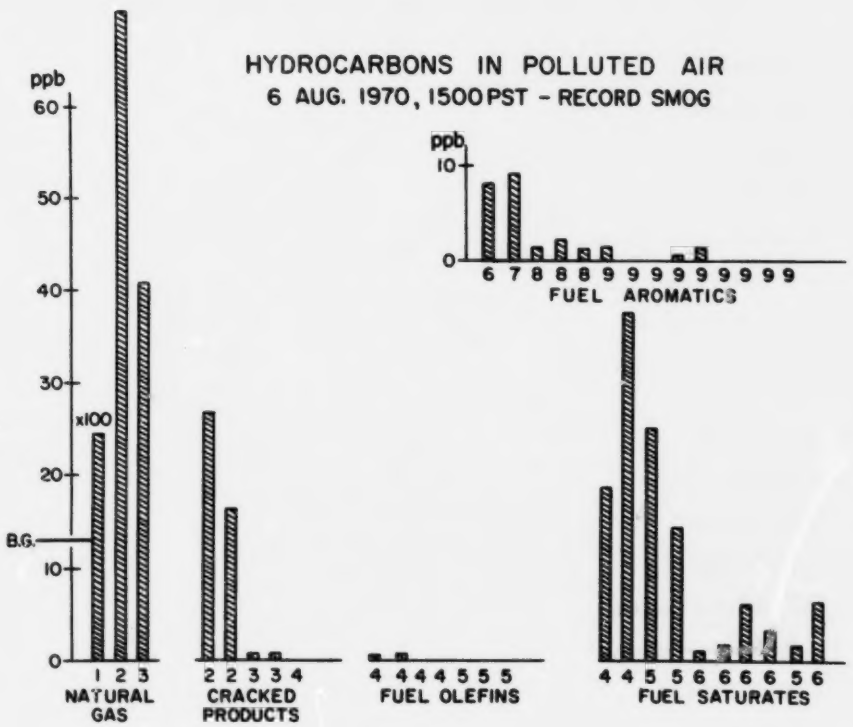


FIGURE 11

TABLE 6

HYDROCARBONS

(By carbon number in the order plotted in bar charts)

Natural Gas (mostly from leaks in natural gas supply pipes)

1. Methane
2. Ethane
3. Propane

Cracked Products (mostly from auto exhaust, not present in gasoline)

2. Acetylene
2. Ethene
3. Propene
3. Me-acetylene
4. 1,3-butadiene

Fuel Olefins (part of the C4's are also derived from cracking)

4. 1-butene
4. isobutene
4. trans-2-butene
4. cis-2-butene
5. 2 me-butene-1
5. trans-2-pentene
5. 2 me-butene-2

Fuel Saturates

4. isobutane
4. n-butane
5. isopentane
5. n pentane
6. 2,2 di-me-butane
6. 2,3 di-me-butane
6. 2 me-pentane
6. 3 me-pentane
5. cyclopentane
6. n-hexane
N naphthenes

TABLE 6 (continued)

Fuel Aromatics

6. Benzene
7. Toluene
8. Ethyl benzene
8. p-xylene
8. m-xylene
8. o-xylene
9. Isopropyl benzene
9. n-propyl benzene
9. p-ethyl toluene
9. m-ethyl toluene
9. o-ethyl toluene
9. 1,3,5-trimethyl benzene
9. 1,2,4 trimethyl benzene
9. 1,2,3 trimethyl benzene
10-12. Higher aromatics

The first three paraffins are listed in the figure as natural gas since leakage of this hydrocarbon mixture seems to be the principal source for these compounds. The "cracked products" are five compounds not found in gasoline but present in auto exhaust in substantial quantities. These form a unique tracer for exhaust gas, since there are few other significant sources of these five compounds, and also a useful indicator of degree of reaction since they present a spectrum of reactivities. The other three groups are listed as fuel components because they are present in gasoline. Small amounts of some of these are produced in engines: in particular the four carbon olefins.

The distribution of hydrocarbons shown here resembles auto exhaust with natural gas and gasoline vapor added. This breakdown will be discussed in more detail in subsequent paragraphs.

Background Hydrocarbons

With the exception of methane, all the hydrocarbons shown in Figure 11 are at far higher concentrations than are found in unpolluted air. To measure background levels, two groups of samples were taken during March 1968 in the San Bernardino and San Gabriel Mountains of southern California during moderate to fresh Santa conditions. These winds blow for several days at a time across southern California from the large desert areas to the north and east and bring the cleanest air to Riverside, California. These samples were taken 1000 to 1300 meters above sea level, one set on the northern slopes of the San Bernardino Mountains and one set in the San Gabriel Mountains. The results are summarized in Figure 12. The levels of methane were satisfactorily consistent and gave an average of 1.39 ppm of methane as shown in Table 7.

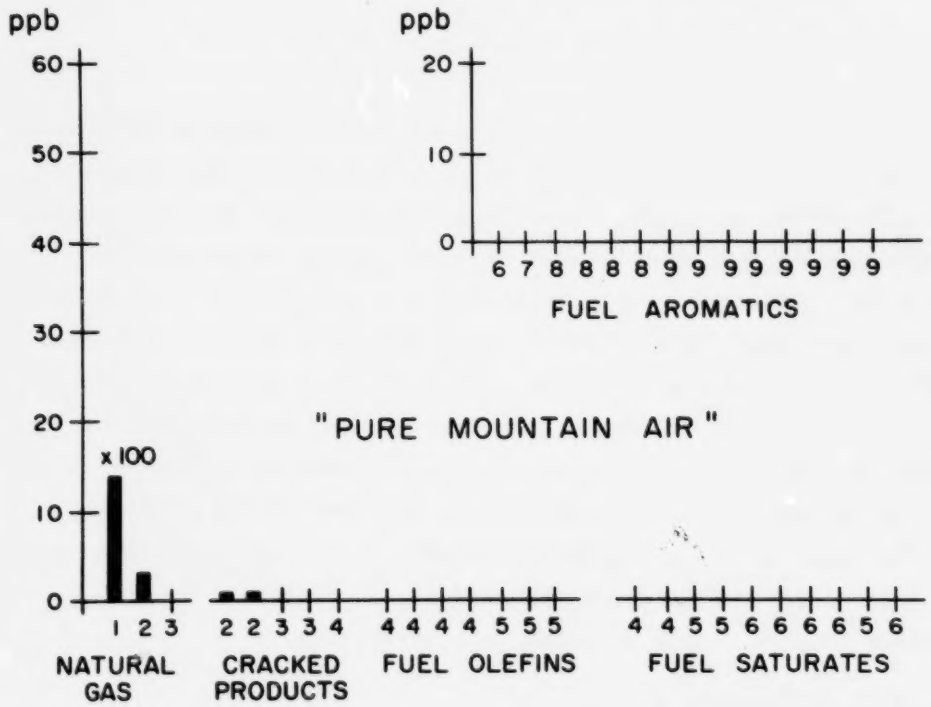


FIGURE 12

To determine whether some of the observed methane concentration might be due to contamination from upwind automotive or natural gas sources, three of the March 19 samples were analyzed for C_2 hydrocarbons. Auto exhaust contains methane, ethene and acetylene in roughly equal amounts so that the maximum possible methane contribution by exhaust gas can be estimated from the amounts of these two unsaturated hydrocarbons present in a sample. Natural gas contains about fifteen times as much methane as ethane, permitting the estimation of the maximum amount of methane contribution from this source.

Three ppb of ethane were present in the three samples, suggesting a possible methane contamination of 0.045 ppm, if the contamination came from natural gas sources. One ppb each of ethene and acetylene were present, suggesting a possible methane contamination of 0.001 ppm, if contamination came additionally from automotive sources. In either or both events, the addition to the methane concentrations given in Table 7 could not exceed 0.046 ppm, or a reduction of 3.3%. Whether the presence of ethane, ethene and acetylene in these samples represents low-level contamination, or whether they too exist in a background concentration is open to further examination.

Our value of 1.39 ppm methane can be converted into the spectroscopist's units by assuming that this concentration prevails from sea level to outer space. Taking the pressure as one atmosphere and the temperature at 273°K, we calculate a value of 1.11 cm for the equivalent layer of methane. This agrees exactly with the figure reported by Fink et al.[2] from their spectroscopic studies, but is slightly smaller than the 1.2 cm reported by Goldberg and Muller.[3]

Table 7 Methane in clear mountain air.

Date	Column	Samples	C ppm	σ%	K mv/ppm*
3/11	Porapak N	11	1.40	1.82	4.54, 4.59
	Alumina	2	1.39		5.07
3/19	Porapak N	12	1.38	2.06	4.65

* K-calibration factor, peak height, for separately prepared mixtures.

Unreacted Air

The sample shown in Figure 11 had obviously undergone considerable photochemical reaction so it was of interest to obtain distributions under unreacted conditions. This can be done by taking samples under the proper weather conditions. On some occasions, particularly during the winter months, winds from the desert will purge the Riverside area of all pollution in the late afternoon or early evening. Such winds often die down during the night so that, with a clear sky overhead, a radiation inversion will form. This will effectively trap pollution overnight and during the early morning traffic rush. Samples taken during this time have not been exposed to sunlight and can yield information on the composition of genuine unreacted air pollution. In the past 10 years, samples have been taken on perhaps a score or more of such mornings. The most striking observation is that typically there are no manifestations of pollution observable (haze, eye irritation, odor, etc.). Yet chemical analysis shows high levels of many pollutants. Hydrocarbon distribution on such a morning is shown in Figure 13.

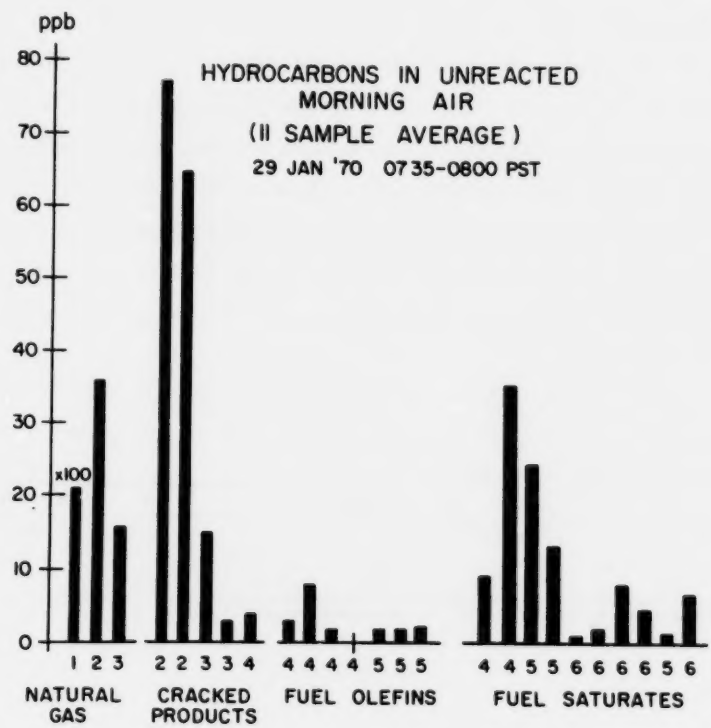


FIGURE 13

Several features of this chart are noteworthy:

1) Concentrations for the most part are as high or higher than those found even in heavy smog. Acetylene, for example, was 78 ppb compared to 27 ppb on August 6, 1970. Since auto exhaust is by far the largest source of acetylene, this indicates that auto exhaust was present in high concentration even though there were no visible signs of pollution.

2) Some very reactive hydrocarbons were present in readily measurable amounts, such as 2.5 ppb of 2-methylbutene-2. The amounts of propene and ethene as compared to acetylene are much higher in this unreacted sample. This will be discussed in much detail later.

3) The amounts and distribution of the saturates are not much different between morning and afternoon samples.

It is tempting to suggest following the course of smog development on such a day. This cannot be done since the radiation inversion is destroyed early in the morning before very much reaction has occurred. Very often little or no oxidant is formed on such days.

The data shown in Figure 13 are averages of 11 samples taken in pairs between 0735 and 0800. Study of individual samples is also informative because it shows that some pairs of individual hydrocarbons fluctuate with each other while others do not. This clearly reflects the different sources of hydrocarbons. Figure 14, for example, shows the fluctuation with time of methane and acetylene. From the duplicate analyses it can be seen that these fluctuations are much larger than the analytical error. Even at 0735 PST the acetylene was higher than in smog samples of 24 October 1968 and 6 September 1968, which in turn are much higher than in clean air.

The independent time fluctuations suggested plotting acetylene and ethene against methane (Figure 15). Although there is some tendency for higher values to go together the correlation is poor. Much better correlations were found when ethene and propene were plotted against acetylene (Figure 16) and when ethane and propane were plotted against methane (Figure 17). The good correlations shown by these two figures reflect the fact that most of the ethene, propene and acetylene come from one source (auto exhaust) while the methane, ethane and propane

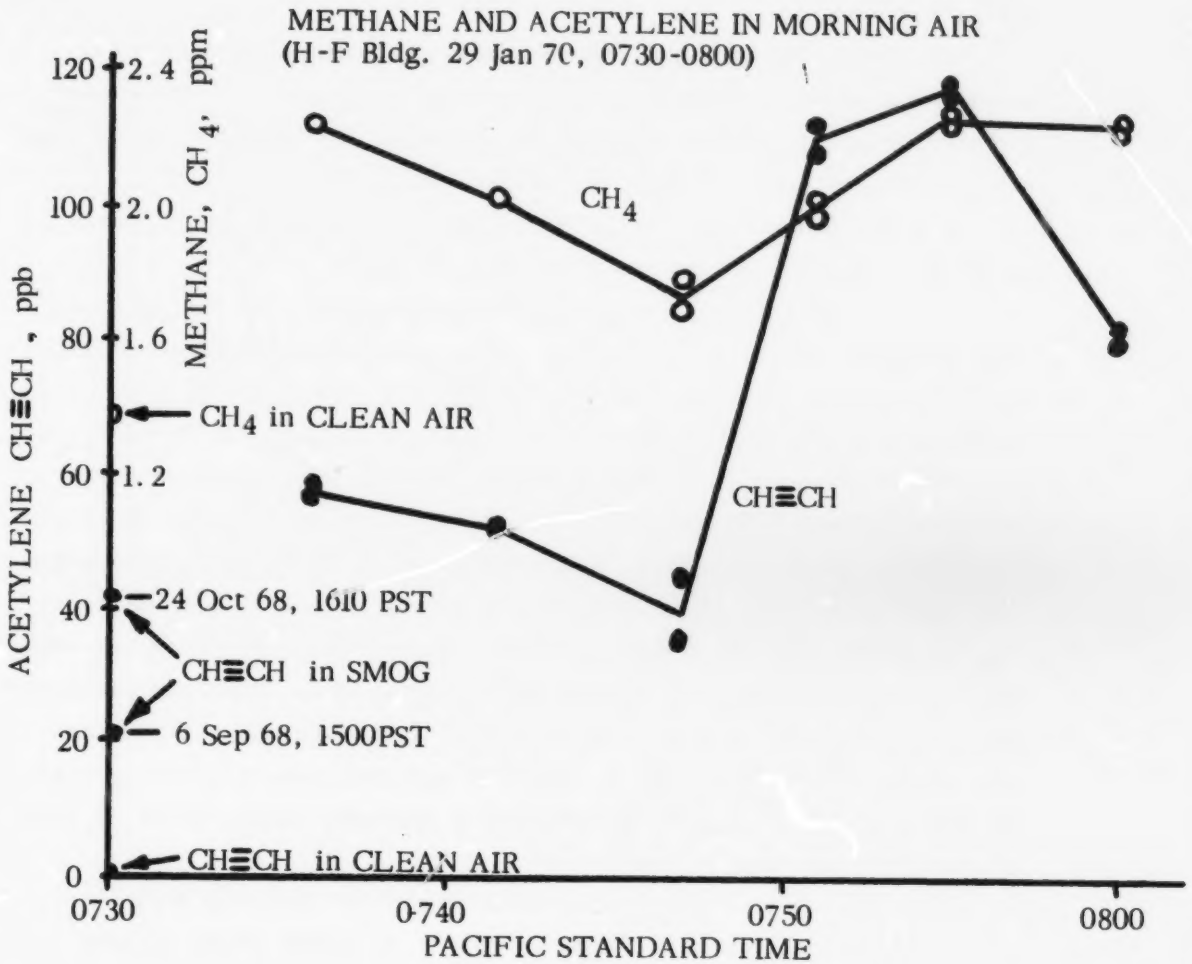

METHANE AND ACETYLENE IN MORNING AIR
(H-F Bldg. 29 Jan 70, 0730-0800)
ACETYLENE CH≡CH, ppb
METHANE, CH4, ppm
120
100
80
60
40
20
0
2.4
2.0
1.6
1.2
CH4
CH≡CH
CH4 in CLEAN AIR
24 Oct 68, 1610 PST
CH≡CH in SMOG
6 Sep 68, 1500PST
CH≡CH in CLEAN AIR
0730
0740
0750
0800
PACIFIC STANDARD TIME

FIGURE 14

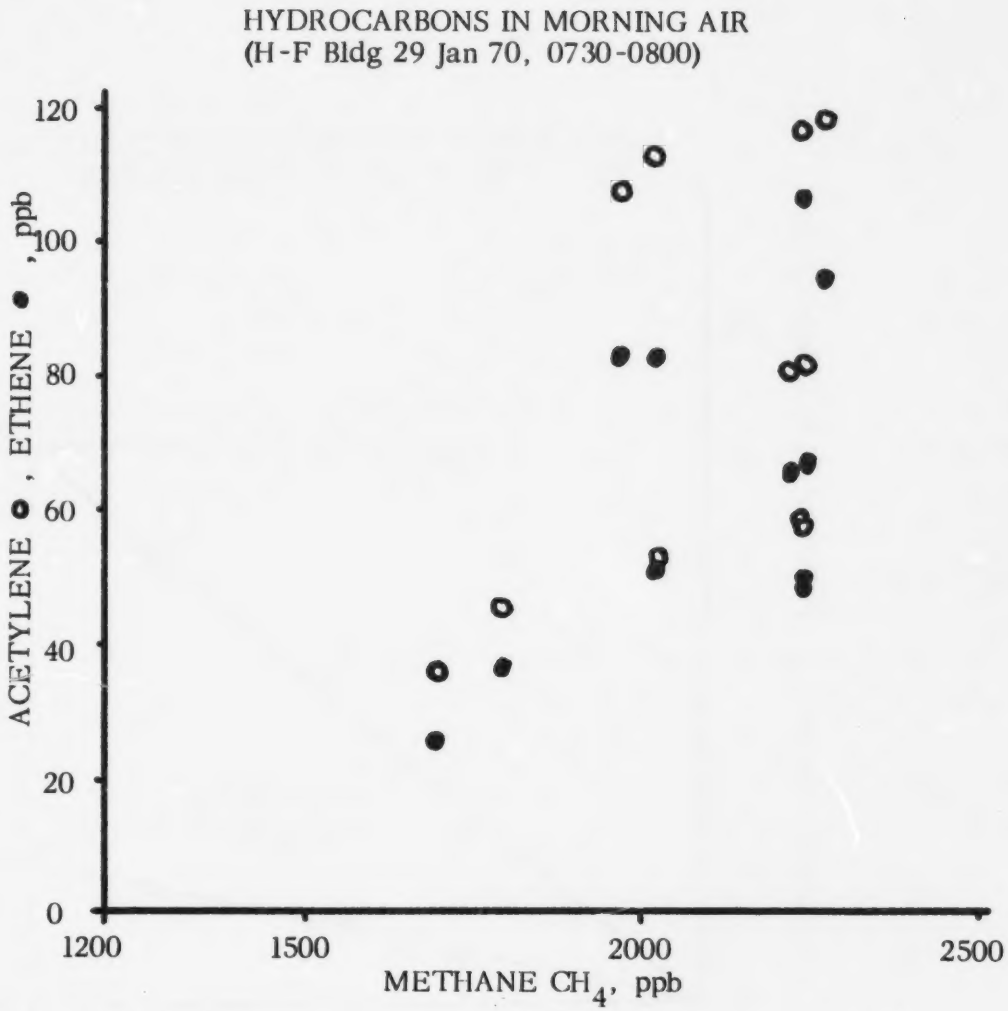

HYDROCARBONS IN MORNING AIR
(H-F Bldg 29 Jan 70, 0730-0800)
ACETYLENE ○, ETHENE ●, ppb
120
100
80
60
40
20
0
1200
1500
2000
2500
METHANE CH_4, ppb

FIGURE 15

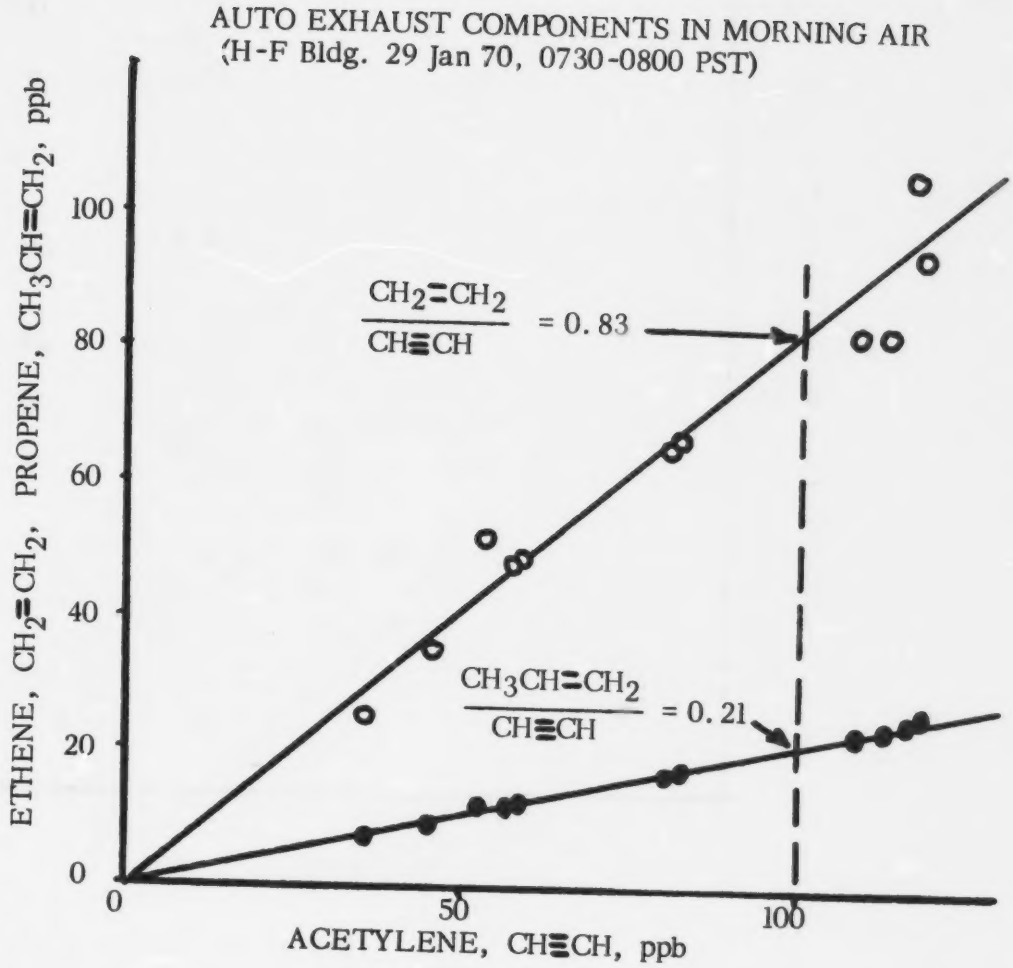
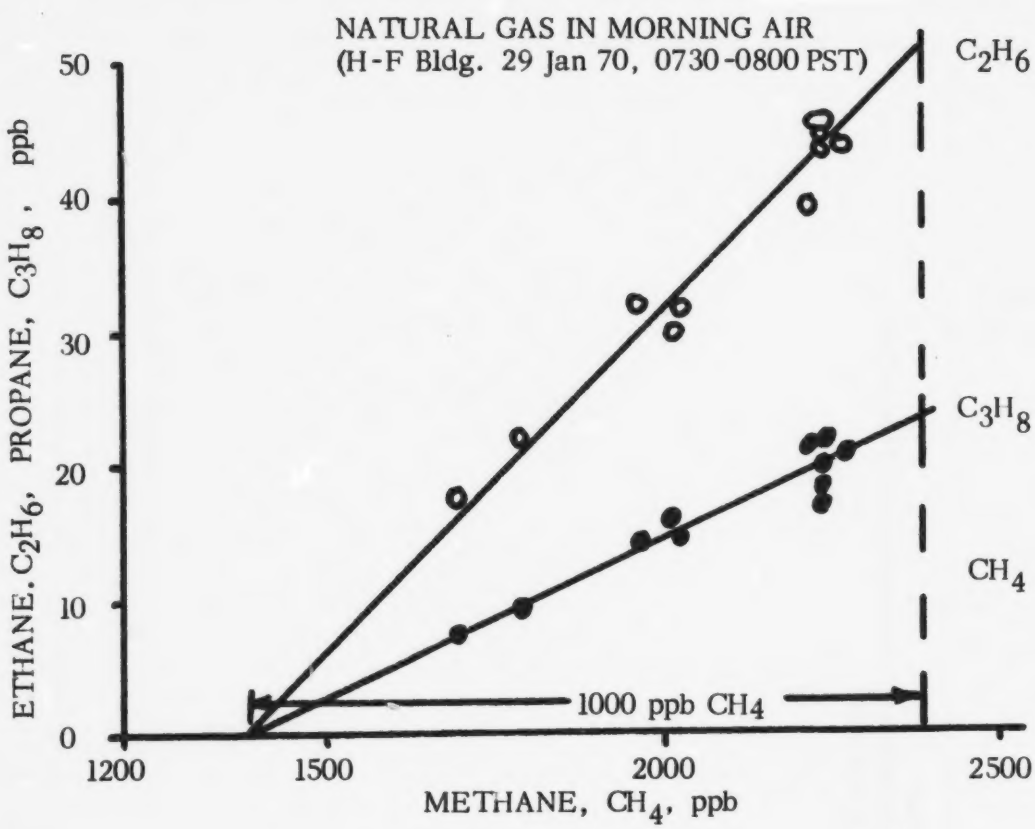

AUTO EXHAUST COMPONENTS IN MORNING AIR
(H-F Bldg. 29 Jan 70, 0730-0800 PST)
ETHENE, $CH_2{=}CH_2$, PROPENE, $CH_3CH{=}CH_2$, ppb
100
80
60
40
20
0
0
50
100
ACETYLENE, $CH{\equiv}CH$, ppb
$\frac{CH_2{=}CH_2}{CH{\equiv}CH}$ = 0.83
$\frac{CH_3CH{=}CH_2}{CH{\equiv}CH}$ = 0.21

FIGURE 16



	ppb	%
C_2H_6	51	4.7
C_3H_8	23	2.1
CH_4	1000	93.2
	1074	100.0

FIGURE 17

come from another. The fact that concentrations vary by a factor of 2-1/2 (saturates) or 5 (unsaturates) indicates that the sources are all relatively local. If these had been carried from a distant source over a period of hours a much more uniform mixture would be expected.

The paraffins (Figure 17) plots both can be extrapolated to zero concentration at about 1350 ppb on the methane axis. This agrees with the value for pure air already cited. The proportions of ethane and propane as compared to the excess methane above this background value can be derived from the slopes of the two plots. The composition shown in the figure approximates that of natural gas (Figure 18).

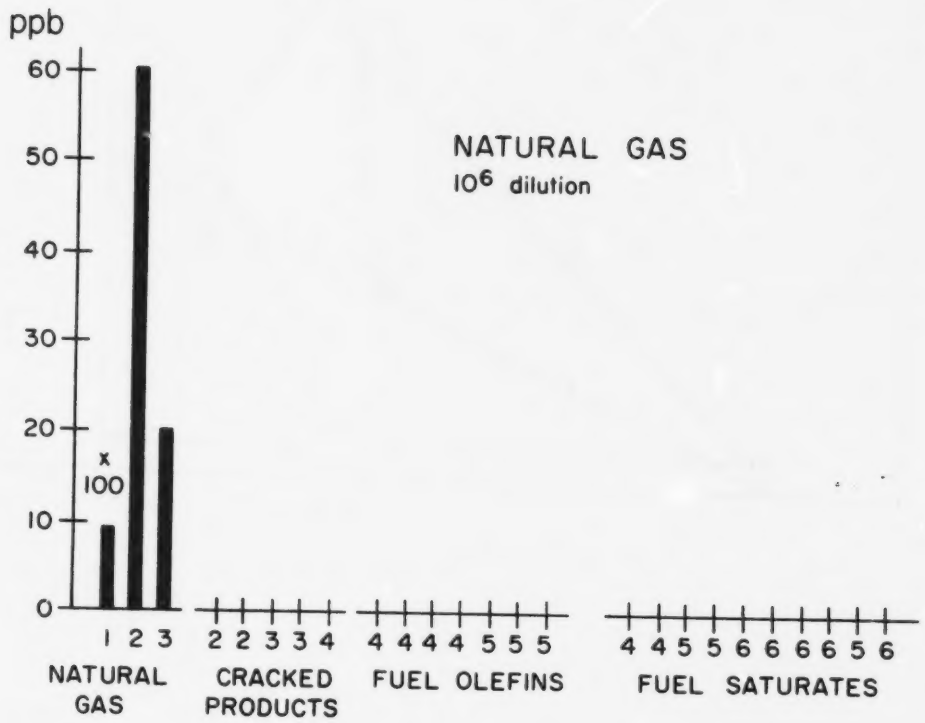


FIGURE 18

TABLE 8. Natural Gas in Ambient Air

	Natural Gas	29 Jan 70	Jan 63		Jan 68
Methane (excess above background)	90	93.2%	91.6	91.3	91
Ethane	8.4	4.7%	7.1	6.8	6.5
Propane	1.7	2.1%	1.4	1.9	2.6

Compositions derived in this way on a number of different occasions are compared in Table 8. The agreement is close enough to be convincing, although natural gas composition varies from week to week and a more detailed study would take this into account.

The plot of ethene and propene versus acetylene has been repeated on a number of occasions. The slopes of these lines can be used to estimate the relative amounts of ethene and propene as compared to acetylene in unreacted air. These ratios are remarkably consistent as shown by the computation made over the years in Table 9. These ratios of 0.85 = ethene/acetylene and 0.25 = propene/acetylene are close to the ratios of 0.91 and 0.34 reported by Neligan et al. in 1961 (Figure 19) for auto exhaust.

TABLE 9. Molar Ratio of Ethene (C_2H_4) to Acetylene (C_2H_2) and Propene (C_3H_6) to Acetylene in Various Samples of Unreacted Air

	Jan 63		22 Dec 65[a]		3 Mar 66	10 Mar 66	
Ethene / Acetylene	0.87	0.95	0.43		0.73	0.84	0.80
Propene / Acetylene	0.22	0.21	0.11	0.16	0.21	0.23	0.22

	24 Oct 66		Dec 67		Dec 67[b]
Ethene / Acetylene	0.91	0.96	0.72	0.72	0.66
Propene / Acetylene	0.25	0.25	0.21	0.21	0.18

TABLE 9 (continued)

	23 Jan 68	29 Jan 70	10 Feb 71
Ethene / Acetylene	0.81	0.83	0.73
Propene / Acetylene	0.24	0.21	0.21

(a) Very high acetylene, two propene instruments

(b) Monterey-Salinas area

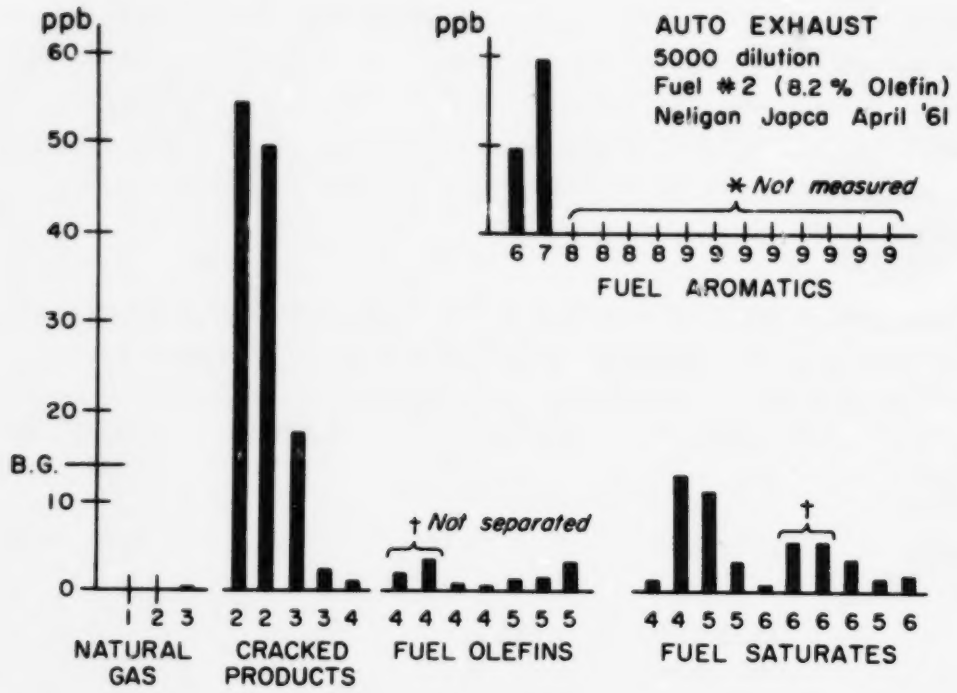


FIGURE 19

In view of the uncertainties in the driving cycle, the values derived from ambient air data are thought to be a truer estimate of the ratios of these components in urban auto exhaust. Figure 19 was plotted on the same scale as the ambient air charts by applying a 5000 fold dilution factor. The 8.2% olefin fuel used to produce this exhaust, when diluted by 10 million to one yieldsthe bar chart of Figure 20.

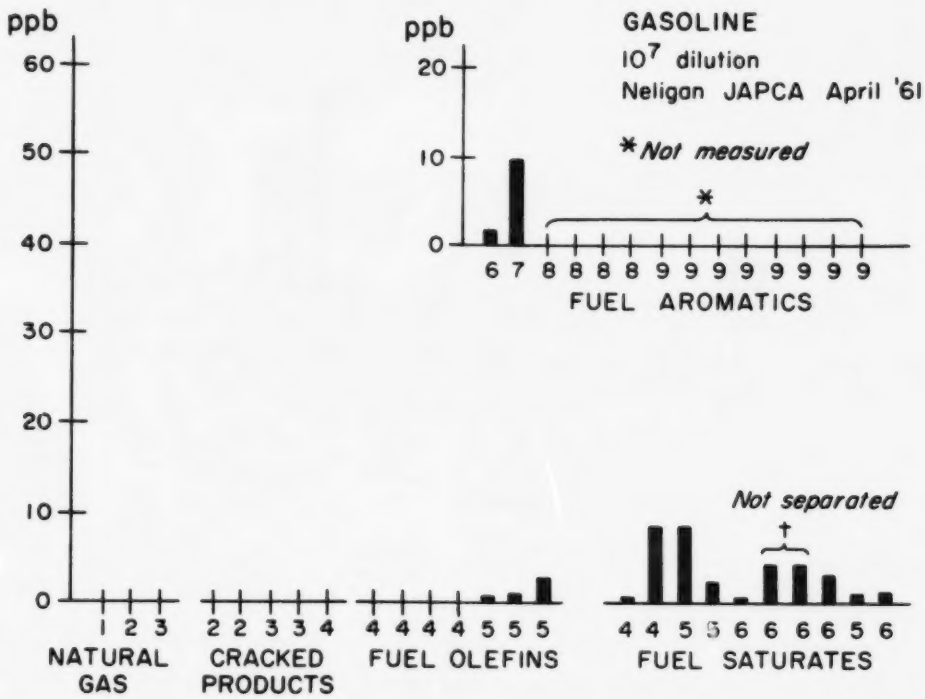


FIGURE 20

This illustrates the reason for classifying these hydrocarbons as fuel components and cracked products. For completeness a partial blowby analysis is shown in Figure 21 . It would obviously be very difficult to distinguish blowby hydrocarbons from exhaust hydrocarbons.

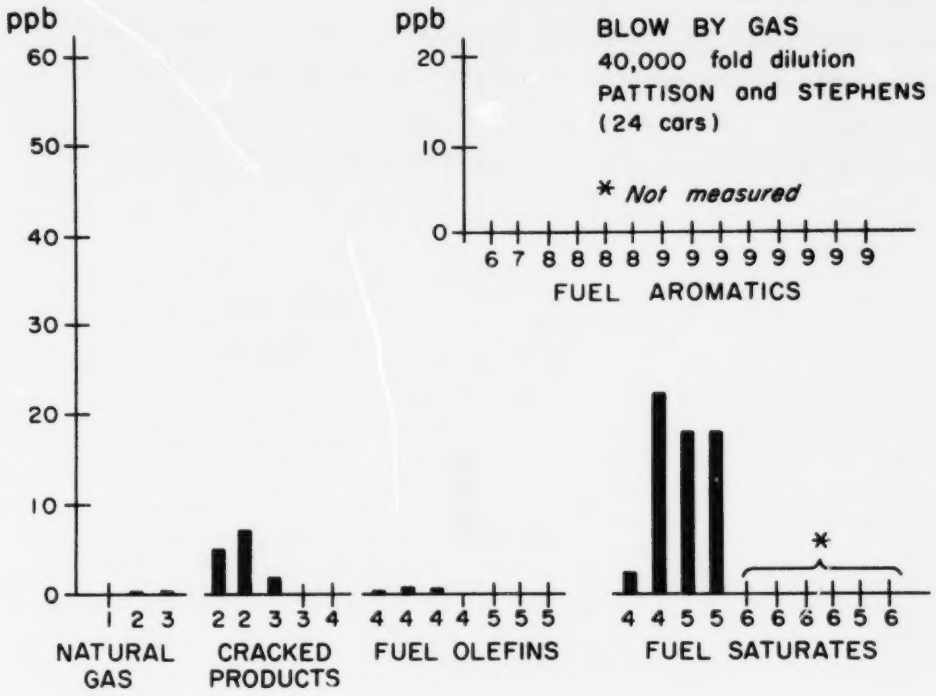


FIGURE 21

Other Sources

Several other hydrocarbon sources were studied as possible contributions to atmospheric hydrocarbon. Figure 22 shows a sample taken in a controlled experimental burn of mountain brush. Three things are noteworthy: (1) The smoke contains very little saturated hydrocarbons of four or more carbons; this is a striking contrast to auto emissions. (2) Concentrations were not very high compared to car exhaust, even though this sample was taken in dense smoke. (3) Ethene was much larger than acetylene again in sharp contrast to auto exhaust.

Figure 23 shows an analysis (at 10 fold dilution) of air from an oil field. This sample was taken just adjacent to oil wells in an urban area. The concentrations of cracked products are attributed to auto exhaust from nearby traffic and the fuel saturates and natural

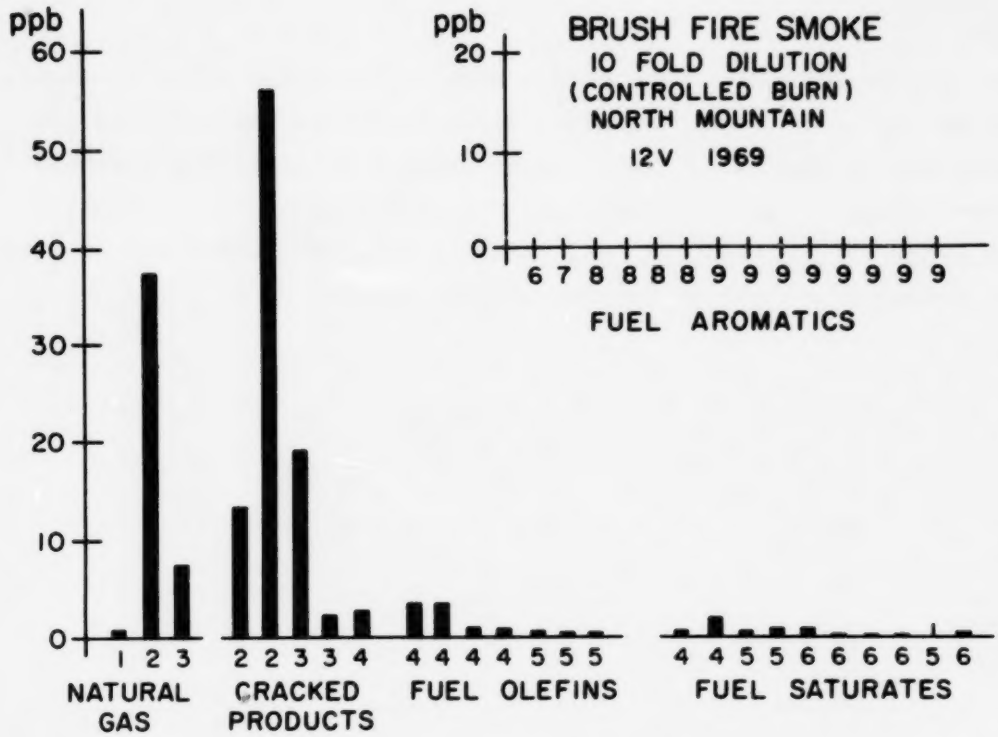


FIGURE 22

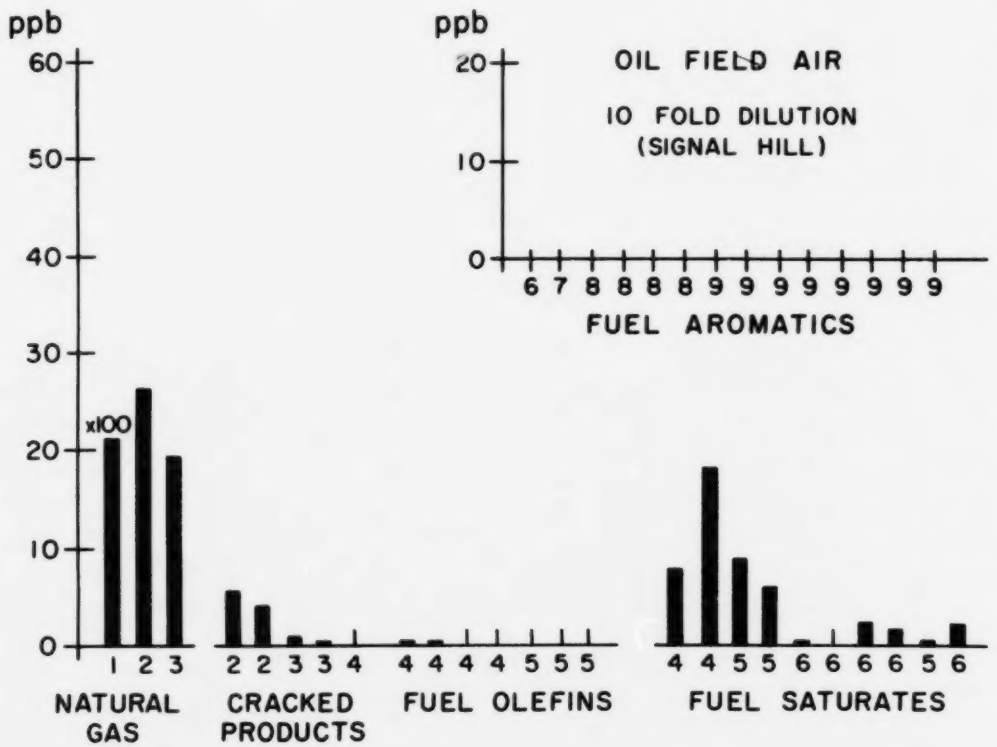
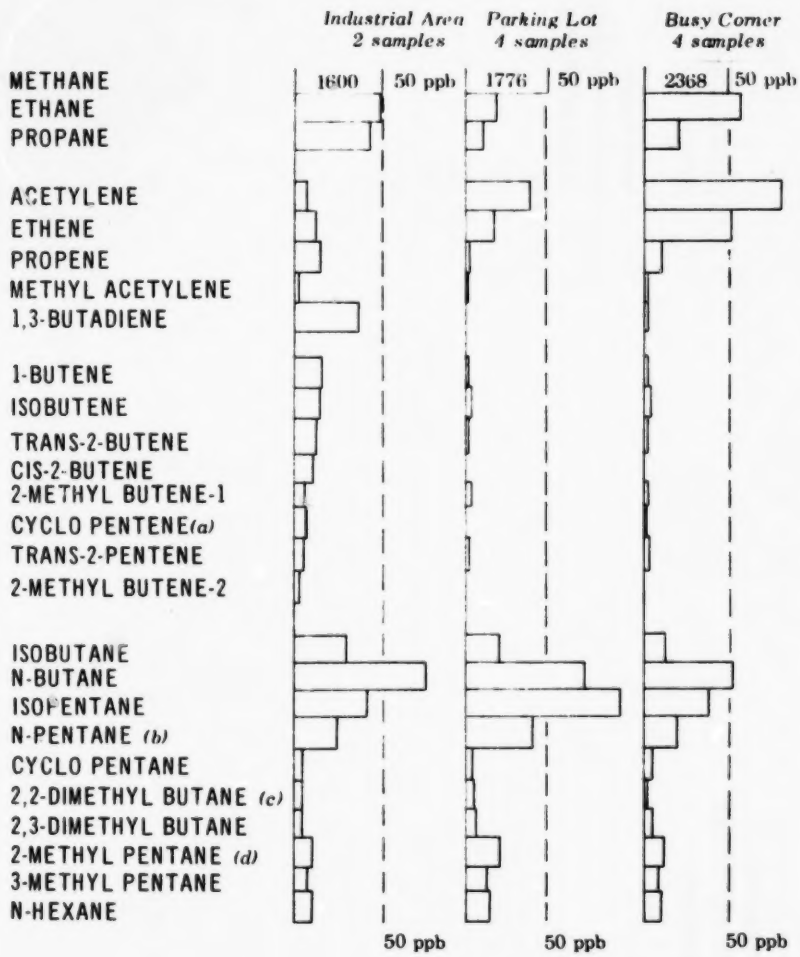


FIGURE 23

gas components present in unusually high concentration are attributed to the oil wells. These emissions may help explain the high levels of paraffins in urban air. Some samples taken in an industrial area are shown in Figure 24 . The most striking difference is the presence of 30 ppb of 1,3-butadiene and a reversed order of abundance of propene, ethene and acetylene (as compared to auto exhaust).



HYDROCARBON DISTRIBUTION NEAR SOURCES.

FIGURE 24

In addition to the propane the four and five carbon paraffins are found in Riverside smog in larger concentrations than are easily accounted for by auto exhaust. For example, in Figure 25 the

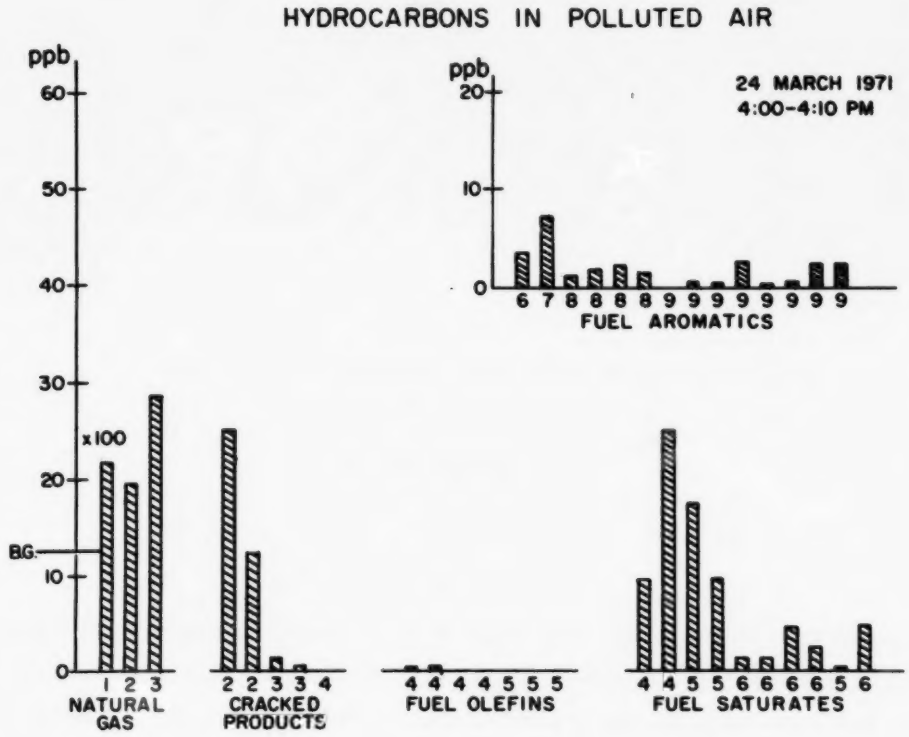


FIGURE 25

n-butane concentration is approximately equal to the acetylene, whereas, in auto exhaust, Figure 19 , it was three or four times smaller. These excesses are ascribed to gasoline vaporized from fuel tanks which is known from emission inventories to be a substantial source of hydrocarbons. It might be expected that gasoline vaporization would be greater on very hot days and there is in fact a striking correlation between maximum oxidant and maximum temperature. Data for one month each in the summers of 1967 and 1972 are shown in Figure 26. It is difficult to see how this trend could be blamed directly on the

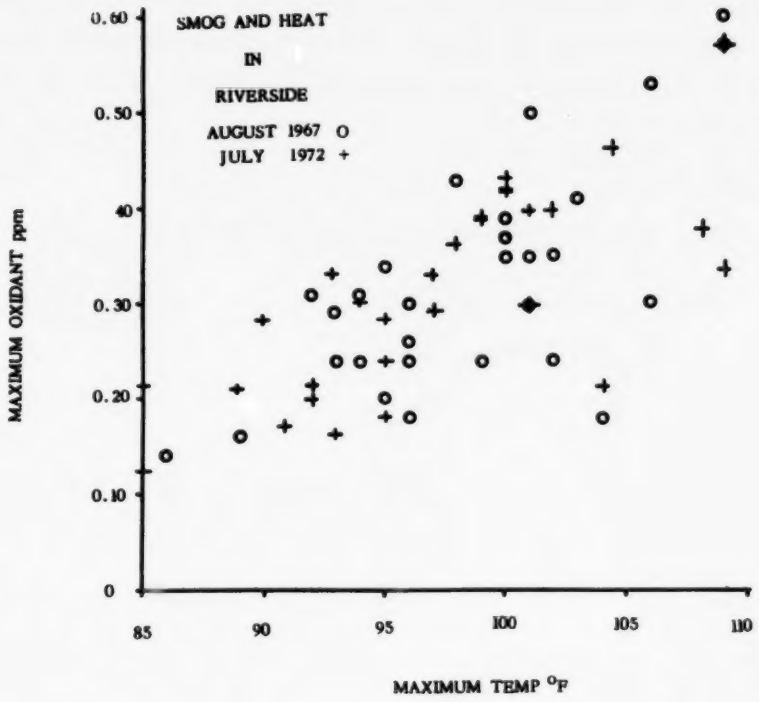


FIGURE 26

effect of temperature on the kinetics of the reaction since most reactions have small activation energies. Several explanations are possible, involving interaction with meteorological variables. For example, high temperatures decrease the relative humidity which will desiccate the aerosol and thereby reduce the scattering of short wave ultraviolet which is crucial for oxidant formation. Also, high temperatures occur when the mixing layer is shallow and is capped by a very warm layer of air aloft. Such conditions could favor prolonged irradiation which also promotes oxidant formation.

To see whether extreme temperatures would be accompanied by excess emissions of light paraffins samples were taken when the temperature was 106°F (see Figures 27 and 28). Six samples were taken simultaneously at each of two locations: 1) the roof of the sixth floor, Health-Finance Building, in central Riverside, and 2) a small hill about four miles east of this and just behind the UCR campus. The UCR air monitoring station

recorded 0.30-0.33 ppm oxidant at this time, so there was moderate smog. Individual samples of each group were nearly the same in distribution, but the central Riverside samples were uniformly higher than the hill samples in all components as though dilution were the only difference between the two sites. Both showed the depletion of the olefins, indicating a substantial degree of reaction.

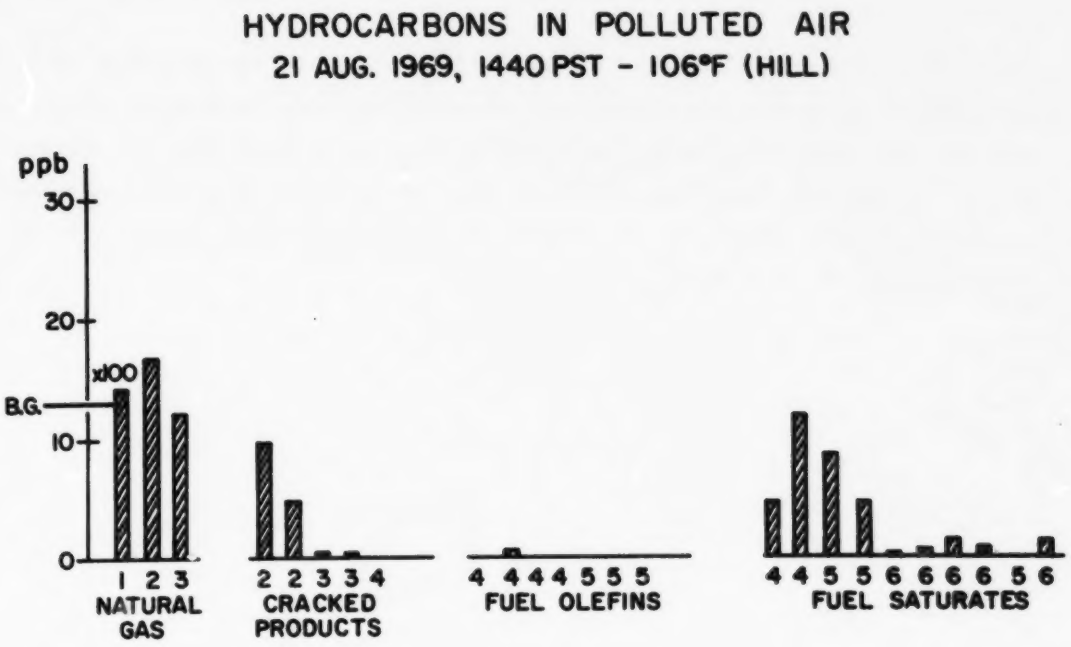


FIGURE 27

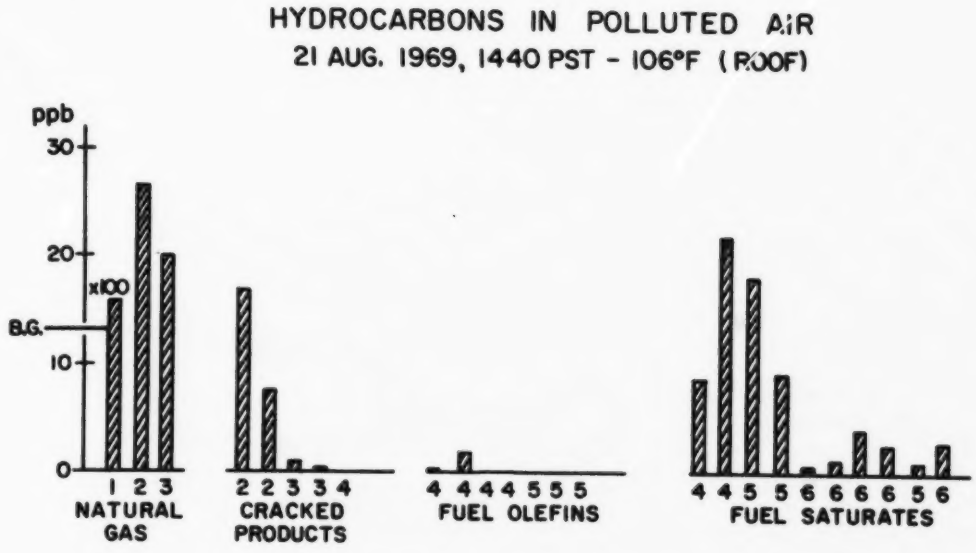


FIGURE 28

If compared with the auto exhaust analysis of Figure 19 , a dilution of 25,000 is indicated for the hill samples. But the result of this experiment was negative; no dramatic increase in C_4-C_5 paraffins as compared to the cracked products was seen (even at 106°F).

Gasoline Vaporization

Nevertheless, these light paraffins are consistently higher in afternoon samples than in morning samples as illustrated in Figure 29. Since these paraffins along with benzene and toluene react to only a

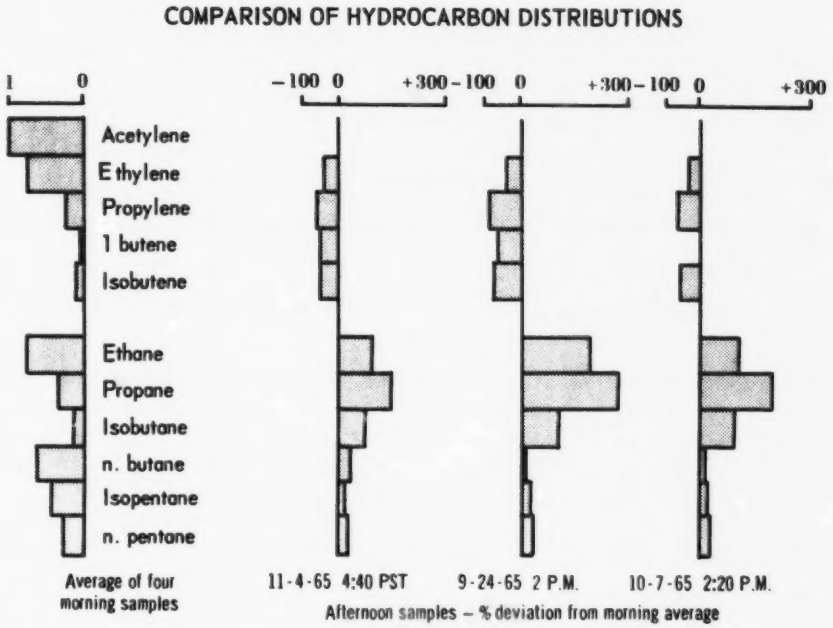


FIGURE 29

small degree (see later sections), it was possible to make an estimate of the contribution of gasoline vaporization to total hydrocarbon by fitting atmospheric data to Raoult's law for gasoline. Raoult's law

was shown to be reasonably accurate when applied to gasoline to calculate the true vapor pressure.[4] To apply this to ambient air data, the concentration of the ith hydrocarbon C_i is approximated by an estimated sum of contributions of liquid and vapor

$$C_i = C_{liq} + C_{vap}$$

This can be most easily visualized by imagining that a sample of liquid gasoline (L nanomoles) and a sample of saturated vapor-air mixture from above this gasoline (V nanomoles) has been added to each mole of air. Then the following two equations apply:

$$C_{liq} = x_i L$$

$$C_{vap} = p_i V = x_i P_{io} V$$

where x_i = mole fraction of hydrocarbon i in the gasoline

p_i = vapor pressure (atm) of hydrocarbon i over the gasoline (assume saturation)

P_{io} = vapor pressure (atm) of pure hydrocarbon i

This hypothetical mixture then has a concentration $\hat{C}_i$ of hydrocarbon i

$$\hat{C}_i = x_i L + x_i P_{io} V$$

To fit this to an ambient air analysis these values are subtracted from the observed concentration C_i

$$C_i - \hat{C}_i = C_i - (x_i L + x_i P_{io} V)$$

To obtain a fit, L and V are adjusted to minimize $\Sigma(C_i - \hat{C}_i)^2$ which is, of course, a least squares procedure. With more than 3 or 4 hydrocarbons this becomes a very tedius calculation best suited to the computer. A program for this was written in APL forthe UCR IBM 360/50 as shown in the following pages. The first trials showed that the temperature

```
    ∇ HC;NIN;CIN;PIN;XIN;N;C;X;P;NND;XND;PND;U;UX;PRNT;ND;CX;XX;CPX;XXPP;DETER;DEV;DEVX;XP;XL;XPV;XL;XV
[1]   'ENTER DATA SET NBR'
[2]   NSET←⍞
[3]   'ENTER CODE NBRS FOR HYDROCARBONS'
[4]   NIN←⍞
[5]   'ENTER CONCS (PPB), USE ZERO IF CONC IS NOT GIVEN'
[6]   U←0≠CIN←⍞
[7]   'ENTER MOLE FRACTIONS'
[8]   XIN←⍞
[9]   'ENTER VAPOR PRESSURES (ATM)'
[10]  PIN←⍞
[11]  'ENTER DATE FOR CONCS - APPROX 8 LETTERS'
[12]  DATE←⍞
[13]  'ENTER SOURCE FOR MOLE FRACTIONS'
[14]  SOURCE←⍞
[15]  'ENTER TEMP FOR VAPOR PRESSURES (DEG F)'
[16]  T←⍞
[17]  'IS ANALYSIS OF VARIANCE FOR REGRESSION DESIRED?'
[18]  ANS←⍞
[19]  Y←'YES'
[20]  XPND←0⍴0
[21]  XX←+/X←X←U/XIN
[22]  CX←+/X←C←U/CIN
[23]  CPX←+/C←X←P←U/PIN
[24]  N←U/NIN
[25]  NND←(~U)/NIN
[26]  XND←(~U)/XIN
[27]  PND←(~U)/PIN
[28]  UX←(X≠0)
[29]  XXPP←+/X←X←P←P
[30]  DETER←÷(XX×XXPP)-XXP×XXP←+/X←X×P
[31]  XP←X×P
[32]  XL←X×L←DETER×(CX×XXPP)-CPX×XXP
[33]  DEVX←UX/DEV←C-LV←XL+XPV←XP×V←DETER×(XX×CPX)-XXP×CX
[34] PRINT:'DATA SET=';NSET;10⍴' ';'NBR HYDROCARBONS IN CALC=';⍴N;'   NBR HYDROCARBONS IN SET=';⍴NIN
[35]  25⍴' ';'C(PPB)   X(MF)   P(ATM)  X P(ATM)  X L    X P  V  X L+X P  V   DEV'
[36]  25⍴' ';' I        I       IO      I IO      I      I IO    I   I IO'
[37]  20⍴' ';DATE;'  ';SOURCE;'   ';T;'∘F   ';T;'∘F';36⍴'    (PPB)'
[38]  ' '
[39]  I←0
[40] ENDHC:→(I≥⍴N)/NODATA
```

```
[41]  I←I+1
[42]  HCNAME[N[I];]; 9 3 DFT PRNT←C[I],X[I],P[I],XP[I],XL[I],XPV[I],LV[I],DEV[I]
[43]  →ENDHC
[44] NODATA:→(0=ρNND)/SUM
[45]  I←0
[46]  XLND←XND×L
[47]  LVND←XLND+XPVND←V×XPND←XND×PND
[48] ENDND:→(I≥ρNND)/SUM
[49]  I←I+1
[50]  HCNAME[NND[I];];9ρ' '; 9 3 DFT PRNT←XND[I],PND[I],XPND[I],XLND[I],XPVND[I],LVND[I]
[51]  →ENDND
[52] SUM:SC←+/C
[53]  SP←+/PIN
[54]  SXL←L×SX←+/XIN
[55]  SLV←SXL+SXPV←V×SXP←(+/XP)++/XPND←XPND,0
[56]  AVDEV←(÷ρDEVX)×SDEV←+/(|DEVX)
[57]  ' '
[58]  16ρ' ';'SUM '; 9 3 DFT PRNT←SC,SX,SP,SXP,SXL,SXPV,SLV,SDEV
[59]  79ρ' ';'AVE'; 10 3 DFT AVDEV
[60]  ' '
[61]  30ρ' ';'L=';L;'    V=';V;'    V×SUM[X(I)P(IO)]=';SXPV
[62]  ' '
[63]  →(Y≠ANS)/0
[64]  '     ANALYSIS OF VARIANCE'
[65] ANAL:MSREG←SSREG←+/LV×LV
[66]  ND←(ρN)-2
[67]  F←MSREG÷MSDEV←(÷ND)×SSDEV←+/DEV×DEV
[68]  15ρ' ';'DF';8ρ' ';'SS';11ρ' ';'MS';11ρ' ';'F'
[69]  'REGRESSION      1'; 13 3 DFT PRNT←SSREG,MSREG,F
[70]  'DEVIATION       ';ND; 13 3 DFT PRNT←SSDEV,MSDEV
[71]  →0
```

assumed to obtain P_{io} values was not crucial to the estimate of vapor contribution. This is because all components increase in vapor pressure by a similar factor between, for example 70° and 100°F. For this reason 100°F was used in later trials. The most important and difficult to obtain piece of data is the gasoline composition. The first attempts were made to use a morning hydrocarbon analysis as a fuel composition, and assuming no vaporized gasoline, but these were not too successful. Later an analysis of Los Angeles basin gasoline was made available by the Western Oil and Gas Association. Use of this fuel composition was discontinued when it was realized that its calculated vapor pressure would be only about 7.5 or 8.0 psia. The four and five carbon paraffins are obviously the crucial factor in both the calculation and in determining the fuel vapor pressure. The composition was, therefore, adjusted to give a true vapor pressure by calculation of 0.700 atmospheres at 100°F or 10.3 psia. This is probably just a little high, but it was used to estimate liquid and vapor contributions for a number of samples. A sample computer print-out is shown in Figure 30 . The first column gives the analysis obtained on 6 Aug 1970. The second column gives the fuel composition (mole fraction, labelled 7/10/72 because it was first adopted on that date). This fuel and its vapor are compared in Figures 31 & 32. The third column gives the vapor pressures of the pure hydrocarbons and the fourth gives the contribution of each hydrocarbon to total vapor pressure. The sum of this column gives the calculated true vapor pressure of the fuel which should be about 0.5 psia above the RVP. The requirement that this be a realistic value is the most crucial element in the calculation. It fixes the C_4-C_5 content of the fuel; changes in the higher molecular weight range will have a minor effect on the vapor pressure and on the final result. Column five gives the concentrations of individual hydrocarbons ascribed to liquid fuel and column six gives that ascribed to vaporized fuel. The totals include all those hydrocarbons presumed present in the fuel and in the atmosphere, including those not measured. They do not include the cracked products. Column seven gives the total of column five and six and column eight gives the deviation of column seven, the "best fit" concentrations, and column one, the measured concentrations. The fit

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FIGURE 30

DATA SET=47	NBR HYDROCARBONS IN CALC=18			NBR HYDROCARBONS IN SET=47				
	C(PPB)	X(I)	P(AT)	X P(AT)	X L	X P V	X L+X P V	SQV
	I	I	IO	I IO	I	I IO	I I IO	
	8/6/70	7/10/72	100*F	100*F	(PPB)	(PPB)	(PPB)	(PPB)
ISOBUTANE	18.800	0.020	4.920	0.098	2.146	12.371	14.517	4.283
N-BUTANE	38.400	0.071	3.510	0.249	7.617	31.332	38.949	0.549
ISOPENTANE	25.200	0.033	1.390	0.139	10.622	17.301	27.922	2.722
N-PENTANE	14.400	0.056	1.050	0.059	6.008	7.463	13.471	0.929
2,3-DIMETHYL BUTANE	0.800	0.005	0.673	0.003	0.336	0.423	0.760	0.130
2,4-DIMETHYL PENTANE	1.800	0.012	0.497	0.006	1.237	0.750	2.987	0.497
2-METHYL PENTANE	6.300	0.040	0.483	0.019	4.292	2.328	6.620	0.820
3-METHYL PENTANE	3.400	0.027	0.415	0.011	2.897	1.409	4.306	0.906
2,2,4-TRIMETHYL PENTANE	1.500	0.010	0.673	0.007	1.072	0.248	1.319	0.177
N-HEXANE	6.600	0.023	0.340	0.010	3.111	1.240	4.351	0.249
BENZENE	2.700	0.020	0.267	0.005	2.146	0.671	2.817	6.883
TOLUENE	9.300	0.050	0.070	0.004	5.364	0.440	5.804	0.436
ETHYL BENZENE	1.500	0.018	0.025	0.000	1.931	0.057	1.988	0.488
p-XYLENE	2.500	0.018	0.023	0.000	1.931	0.052	1.983	0.517
M-XYLENE	1.100	0.036	0.022	0.001	3.862	0.108	3.970	2.870
O-XYLENE	1.200	0.018	0.018	0.000	1.931	0.041	1.972	0.772
p-ETHYL TOLUENE	0.600	0.010	0.014	0.000	1.073	0.018	1.090	0.490
M-ETHYL TOLUENE	1.300	0.015	0.014	0.000	1.609	0.026	1.635	0.335
PROPANE		0.001	12.630	0.010	0.086	1.270	1.356	
1-BUTENE		0.001	4.300	0.004	0.107	0.541	0.648	
ISOBUTENE		0.001	4.320	0.004	0.107	0.543	0.650	
TRANS-2-BUTENE		0.001	3.500	0.004	0.107	0.440	0.547	
CIS-2-BUTENE		0.001	3.130	0.003	0.107	0.394	0.501	
2-METHYL BUTENE-1		0.009	1.280	0.010	0.853	1.287	2.140	
TRANS-2-PENTENE		0.008	1.050	0.008	0.858	1.056	1.914	
2-METHYL BUTENE-2		0.008	0.980	0.009	0.859	0.986	1.844	
CYCLO PENTENE		0.002	0.700	0.001	0.215	0.176	0.391	
ISOPROPYL BENZENE		0.010	0.014	0.000	1.073	0.018	1.090	
N-PROPYL BENZENE		0.010	0.014	0.000	1.073	0.018	1.090	
O-ETHYL TOLUENE		0.010	0.014	0.000	1.073	0.018	1.090	
135 TRIMETHYL BENZEN		0.010	0.014	0.000	1.073	0.018	1.090	
124 TRIMETHYL BENZEN		0.015	0.014	0.000	1.609	0.026	1.636	
123 TRIMETHYL BENZEN		0.010	0.014	0.000	1.073	0.018	1.090	
HEPTANES		0.120	0.014	0.002	12.875	0.211	13.086	
OCTANES		0.100	0.100	0.010	10.729	1.257	11.986	
CYCLO HEXANES		0.030	0.207	0.006	3.219	0.756	3.975	
CYCLO HEPTANES		0.013	0.120	0.002	1.395	0.196	1.591	
CYCLO OCTANES		0.003	0.070	0.000	0.322	0.026	0.348	
CYCLO NONANES		0.003	0.050	0.000	0.322	0.019	0.341	
HEXENES		0.030	0.410	0.012	3.219	1.546	4.765	
HEPTENES		0.003	0.130	0.000	0.322	0.049	0.371	
OCTENES		0.002	0.070	0.000	0.215	0.016	0.232	
CYCLO HEXENES		0.003	0.210	0.001	0.322	0.079	0.401	
CYCLO HEPTENES		0.007	0.100	0.001	0.751	0.088	0.839	
10 CARBON AROMATICS		0.015	0.010	0.000	1.609	0.013	1.623	
11 CARBON AROMATICS		0.012	0.010	0.000	1.287	0.015	1.303	
12 CARBON AROMATICS		0.010	0.010	0.000	1.073	0.013	1.085	
SUM	142.800	1.001	47.872	0.700	107.374	87.965	195.339	28.217
				*14.7 =			4V3	1.568
				10.3 psia				

L=107.2882853 V=125.7239706 V*SUM[X(I)P(IO)]=87.96503907

ANALYSIS OF VARIANCE

	DF	SS	MS	F
REGRESSION	1	2851.920	2851.920	506.219
DEVIATION	16	90.140	5.634	

FIGURE 30

Vapor/Liquid Computation

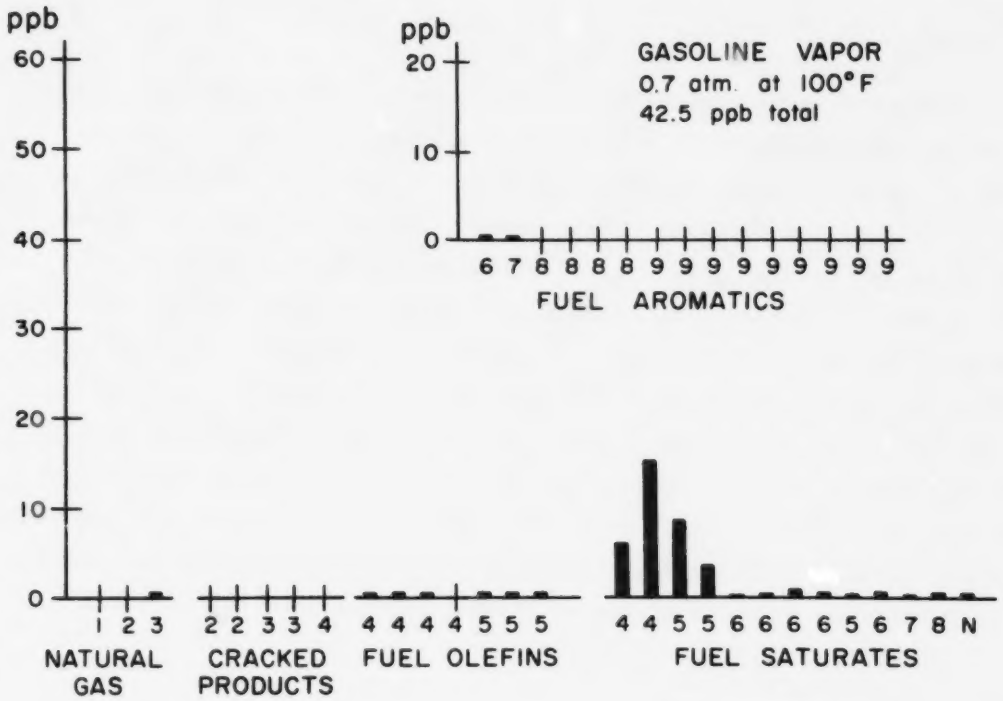


FIGURE 31

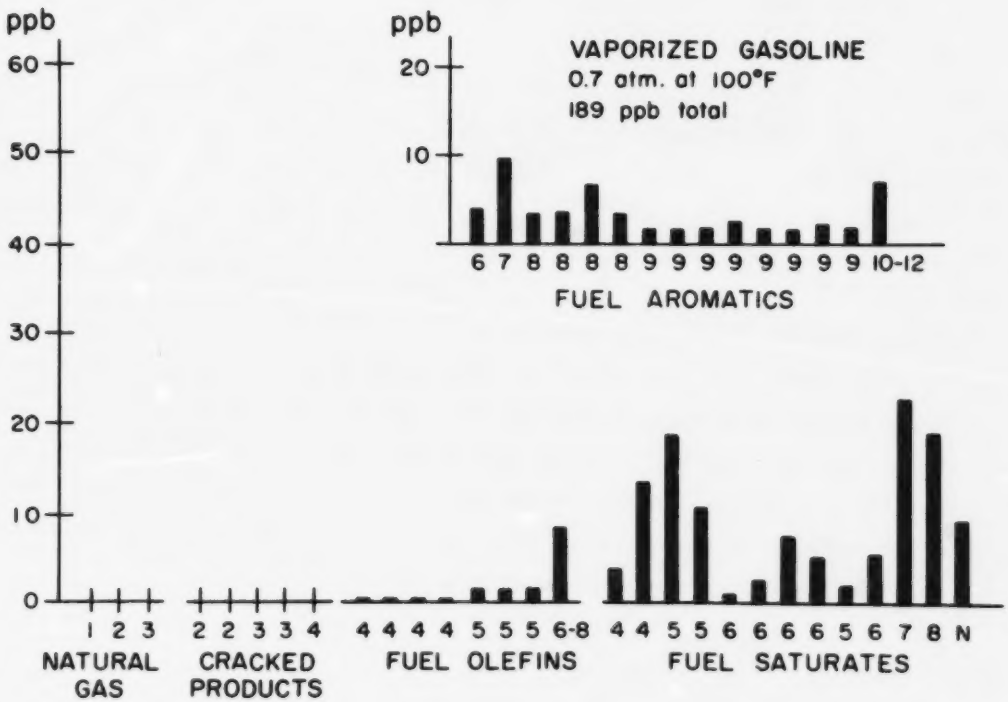


FIGURE 32

in this example is reasonably good; benzene is the poorest fit which may be due to formation of benzene in engines as a cracking product. It is not surprising that vapor accounts for most of the butanes and over half of the pentanes. In contrast, it accounts for only about 2-3% of the xylenes. In comparing the totals derived from liquid and from vapor, it must be remembered that this treatment is "by moles" whereas emission inventories are expressed by weight. If we take the fuel molecular weight to be 100 and the vapor to be 60, then the vapor contribution in the case illustrated is just half the liquid fuel contribution. To this liquid contribution must be added the cracked products found in exhaust gas. This would make the vapor contribution about 30-40% of the exhaust contribution which agrees with the generally accepted emission estimates. Some results obtained on other samples are given in Table 10.

TABLE 10. Hydrocarbons

Sample Date	Oxidant (ppm)	Liquid (ppb)	Vapor (ppb)	V/L
6 Aug 70, afternoon	0.65	107	88	0.82
24 Mar 71, afternoon	-	93	51	0.55
21 Aug 69, roof, afternoon	0.30-0.33	84	48	0.57
21 Aug 69, hill, afternoon	0.30-0.33	34	28	0.82
10 Feb 71, morning	-	189	43	0.23

Hydrocarbons in Other Locations

Since one liter of sample or less suffices to make an analysis for two dozen hydrocarbons, it was possible to analyze samples from a number of locations around the country and around the world. Except for locations in California, samples were taken by willing cooperators to whom bottles were shipped by common carrier. Aside from southern California, the following locations have been sampled:

Bay Area	Honolulu
San Joaquin Valley	Tokyo, Japan
Point Arena	McMurdo Sound (Antarctica)
Salinas Valley	New York
Denver	

Two of these locations, Point Arena and McMurdo, were chosen to estimate the background levels of hydrocarbons, methane in particular. The values found were near or perhaps a little lower than the 1.39 ppm found in the southern California mountains. The levels of ethane, ethene and acetylene were also similar. Several of these groups of samples have been described in previous papers so that discussion will not be repeated here.[5-7] Generally speaking, all these other areas showed hydrocarbon levels and distributions similar to those found in southern California. There was considerably more variation from sample to sample than in southern California. The reasons for this are not known. In spite of it the general impression was that of auto emissions rather than any of the other sources described earlier. Tokyo and Honolulu were of special interest because they have little or no natural gas, although importation of LNG is beginning. As expected, methane values were low (near the background value) and the amounts found might be ascribed to other sources (auto exhaust, fuel combustion). Honolulu probably has poor atmospheric ventilation only on rare occasions. Since our samples were taken on one day only, not necessarily a stagnant air day, this does not constitute a good test of the prediction that the lack of natural gas should lead to methane values near the worldwide background.

Tokyo is of special interest for two additional reasons. It has a very rapidly expanding automobile population (tripled in ten years) and the characteristic symptoms of photochemical smog are increasingly noticeable (oxidants over 0.3 ppm). In addition it has an unusual population of LPG powered vehicles (especially taxicabs). Since propane and propene are major components of LPG exhaust, special attention was paid to these two components in Tokyo air. They were <u>not</u> found in exceptional amounts in Tokyo air. While the proportion of taxis in

Tokyo which run on LPG is unusually high, they nevertheless do not form a large part of the total vehicle population. The Japanese are now using GLC atmospheric hydrocarbon analysis to study their problem.

The New York samples were taken in Manhattan near heavy traffic areas. Concentrations were quite high but remarkably similar to Riverside in distribution. The Denver samples were also more variable than the southern California experience.

HYDROCARBON REACTIVITY

Since the very beginning of research on photochemical air pollution, it has been evident that the reactivities of individual hydrocarbons are strongly dependent on their structure. This is true whether reactivity is judged by chemical criteria such as ozone formation, oxidation of nitric oxide, or hydrocarbon disappearance, or by symptoms such as eye irritation, plant damage, or aerosol formation. The correlation between these measures of reactivity is neither strict nor quantitative but there is a tendency for them to go together. After some investigation, a rather clear pattern of chemical reactivity began to emerge. Compounds which contain double bonds are much more reactive than those which do not. This was apparent first for the olefins and later for the aromatics, some of which proved to be more reactive than olefins of the lowest reactivity. From the nature of the products, it could be inferred that rupture of the double bond occurs in both cases, at least for olefins and polyalkyl aromatics. Benzilic hydrocarbons form a special case (see later). A further parallel appeared in that addition of alkyl groups adjacent to either olefinic or aromatic double bonds increases the reactivity. The number of such alkyl groups is more important than their size. Tetramethyl ethylene is the most reactive compound known and mesitylene (1,3,5 trimethyl benzene) is comparable in reactivity to the less reactive olefins. The paraffins, not having double bonds, react more slowly, although lengthening the chain does increase reactivity, perhaps simply by increasing the number of potential sites for attack. Napthenes, in very limited studies, appear to behave like paraffins. Acetylene is of very low reactivity. These relationships are summarized in Figure 33.

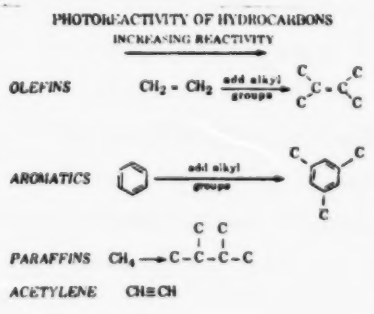


FIGURE 33

Throughout this discussion, the term reactivity is used in its chemical sense; that is, the rate at which the hydrocarbon disappears under simulated atmospheric conditions (diluted along with nitrogen oxides to ppm concentrations in air and irradiated with artificial sunlight). The term reactivity has also been used to mean either the rate at which nitric oxide is converted to nitrogen dioxide under these conditions or the amount of ozone produced. Of course, the formation of objectionable products (eye irritants, plant toxicants, etc.) is the matter of real concern rather than just the disappearance of the hydrocarbon. However, there must be a relation between the two; certainly hydrocarbon which does not react cannot form noxious products. Schemes have been devised for rating hydrocarbons according to their tendency to produce such products. Such a rating is sometimes referred to as "hydrocarbon reactivity" but it would be preferable to reserve this term for its chemical sense and to use a term such as "smog potential" for ratings based on the formation of objectionable products. For the most part those compounds which are of high chemical reactivity are those which also produce noxious products.[8] There are, however, recognized differences in the ability of hydrocarbons of various structure to produce the various symptoms.

So far as is known hydrocarbons of all types are capable of causing the photochemical conversion of nitric oxide to nitrogen dioxide, albeit at vastly varying rates.[9] This reaction is closely related to the formation of ozone, a toxicant of major concern.[10] Compounds which contain double bonds also produce peroxyacyl nitrates, a family of plant toxicants and eye irritants. Saturated hydrocarbons produce little, if any, PAN. Likewise, the enhancement of aerosol formation in systems containing sulfur dioxide has been demonstrated for olefins but not for paraffins. Subjective measurements of eye irritation also show that saturated compounds produce less than unsaturated compounds.

Evaluation of the relative importance of various classes of hydrocarbons in producing photochemical air pollution encounters a further obstacle. Some knowledge of the extent to which various hydrocarbons react under realistic ambient conditions is needed. If very long times are available for reaction, then hydrocarbons of low reactivity may make

a substantial contribution. This is a serious question because the hydrocarbons of low reactivity constitute a large part of the total emissions (paraffins, napthenes, benzene and acetylene). Such emissions can only be retained in the lower atmosphere long enough for reaction to occur if there is a temperature inversion. Under such conditions the cooler air at ground level cannot mix with the warmer air aloft. Such inversions, although they persist long enough to permit photochemical reactions to occur, are vulnerable to the normal heating of the lower atmosphere which results from contact with the warm surface of the earth. There has been no way to estimate the lifetime of such a parcel of stable air, and this determines the effective time available for reaction. The fact that hydrocarbons do vary in reactivity raises the possibility that analysis of polluted atmospheres could provide an answer.

Acetylene, ethene and propene are a unique trio of compounds for judging the extent to which reaction has taken place in an ambient air sample. These three compounds are not present in gasoline but are formed in auto engines and emitted in exhaust gas in substantial quantities. Moreover, they differ significantly in reactivity so that they disappear at different rates under irradiation. The relative amounts of these three hydrocarbons in exhaust gases vary from car to car and are dependent on engine operation as well. But the ratios of the total rates of emission of the three from all the cars in an urban area are probably nearly independent of time, place and circumstance. Evaluation of unreacted samples has lead (see prior sections) to the values of 0.85 for the ethene/acetylene ratio and 0.25 for the propene/acetylene ratio in unreacted emissions (molar basis). To study the effect of photoreaction, we have expressed each of these three hydrocarbons as a percent of the total of the three. Thus ethene comprises $0.85/(1 + 0.85 + 0.25) = 40.5\%$ and propene $0.25/(1 + 0.85 + 0.25) = 11.9\%$ of the total. Expressed in this way the effect of reaction can be studied independently of dilution.

In previous sections evidence was presented that under specially chosen conditions ambient air contains quite high concentrations of unreacted auto exhaust (dilutions of 2000 or so). Table 9 showed

that the relative amounts of acetylene, ethene and propene were quite consistent in unreacted air. The remarkable and revealing fact about these samples is that symptoms of air pollution are completely absent. On one occasion, the evening paper reported "this morning Riversiders awoke to a cloudless sky, and air unmarred by smog, and as a result the mountains stood sharply etched against the horizon."

Ambient Air Irradiation

In spite of this, analysis shows that high concentrations of auto exhaust and natural gas hydrocarbons are present under these conditions. It would seem that monitoring of the air on such a day would provide a particularly simple and useful way to study development of photochemical smog. This is not possible because the radiation inversion which provides this trapping is destroyed by solar heating before the photochemical reaction can proceed very far. In order to study hydrocarbon disappearance under irradiation, it is necessary to trap a sample and then irradiate it, either with artificial or natural sunlight. The results of such an experiment are shown in Figure 34 . Initial concentrations were substantially higher than found in smog; even of those

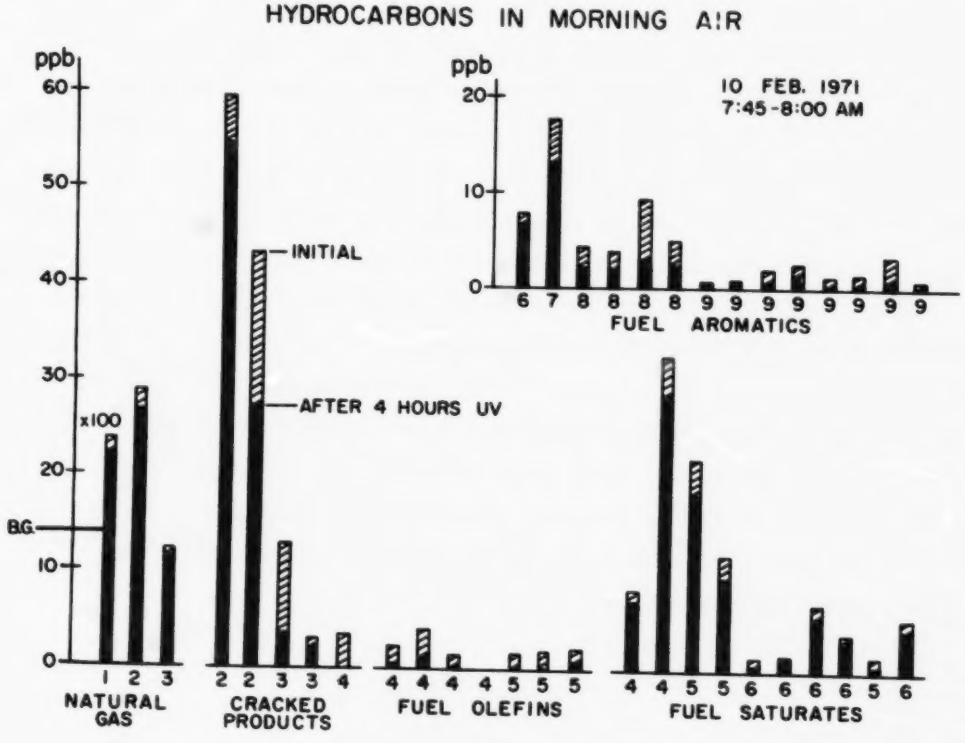


FIGURE 34

hydrocarbons of very low reactivity such as acetylene and the paraffins. The presence of substantial amounts (3-5 ppb!) of some highly reactive compounds (four and five carbon olefins and diolefins) shows that this sample was largely unreacted. The amounts which disappeared in four hours of ultraviolet were quite consistent with reactivities determined in the laboratory studies (see for example, Tuesday.[9]

In four hours about 37% of the ethylene reacted. Although the olefins are most reactive and paraffins least reactive, the quantities present reverse this order. Thus, quantity and reactivity, when multiplied together, become roughly constant. The aromatics are intermediate in both quantity and reactivity. This indicates that very little can be gained by focusing attention on any one group of hydrocarbons. It is also evident that the cracked hydrocarbons (those present in exhaust but not in gasoline) contribute substantially to total reacted hydrocarbons. It should always be kept in mind that substantial additional hydrocarbon in the higher molecular weight range is present but not measured. Presumably, these would follow the reactivity pattern of these respective classes and not change the overall conclusion.

With two 20-liter borosilicate carboys, it was possible to take a pair of ambient air samples simultaneously so that one could be irradiated in artificial sunlight and one in natural sunlight. This was done with a pair of samples taken on October 24, 1966 between 0630 and 0650 PST. These were taken on the roof of a five-story building in central Riverside. This is near downtown traffic but far enough removed to permit mixing. The two samples were nearly identical in composition: one was irradiated in natural sunlight beginning about 0730 PST and the other in artificial ultraviolet the next day. The sky was clear during the entire period of irradiation with natural sunlight.

A portion of the results of photolysis by natural sunlight of one of these samples is shown in Figure 35 , and the comparison sample photolyzed with ultraviolet in Figure 36 . There are several notable features in these plots: the natural sunlight sample showed more reaction than the artificial but the relative reactivities were

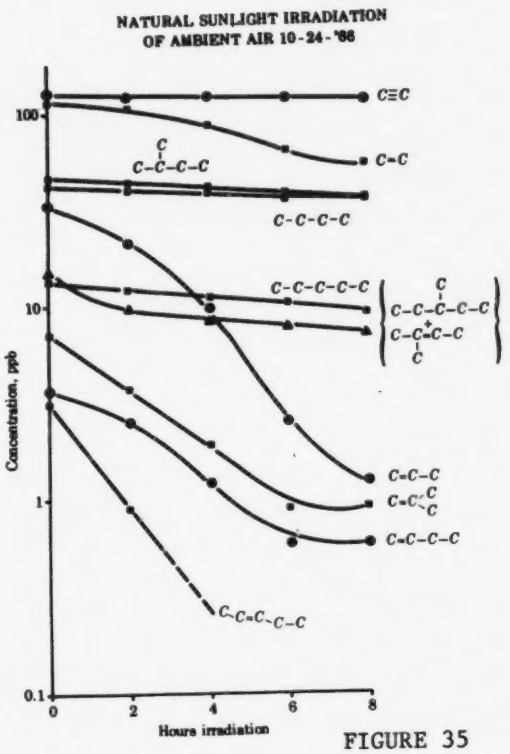


FIGURE 35

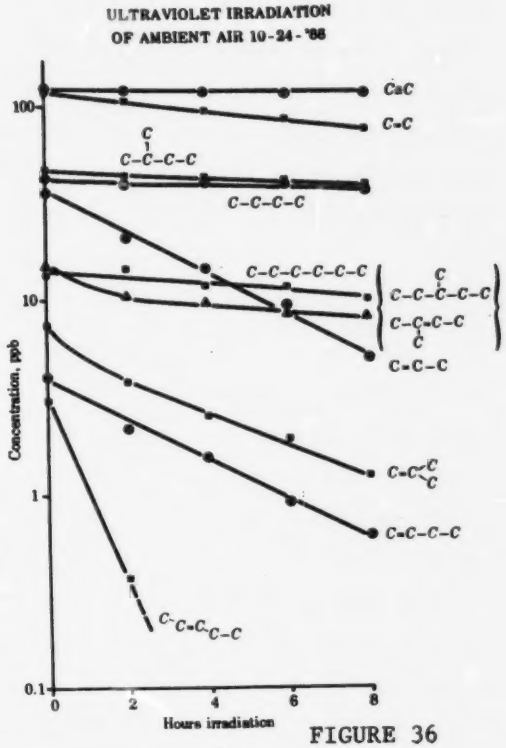


FIGURE 36

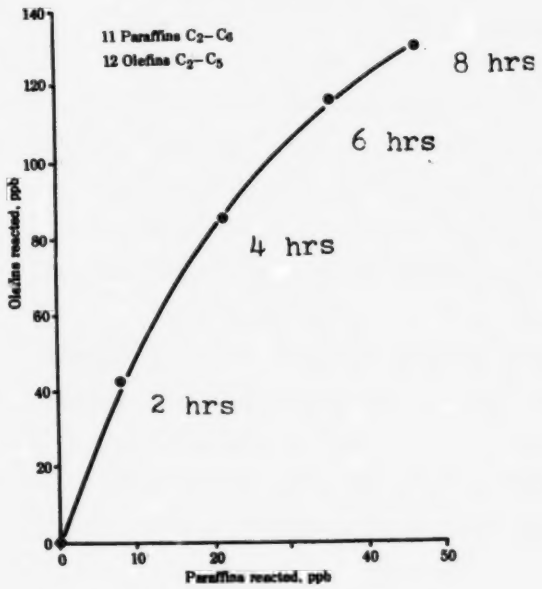


FIGURE 37

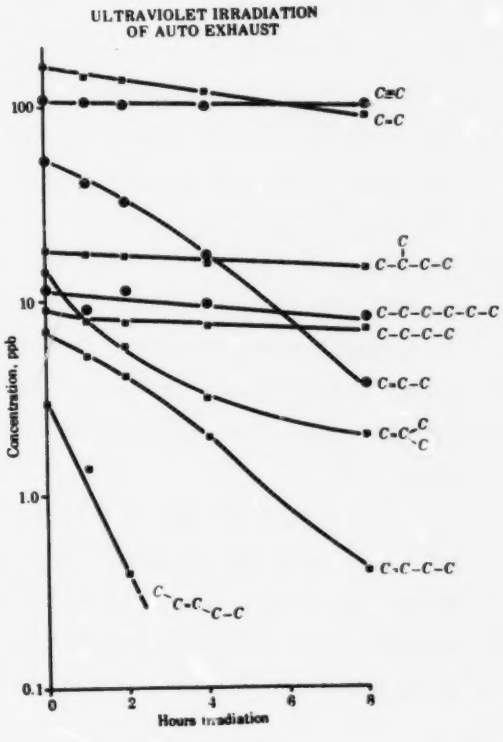


FIGURE 38

very similar. The natural sunlight plots have a maximum slope near noon which reflects the maximum intensity of sunlight. The artificial irradiation lines are nearly straight on these plots of log concentration versus time. This rather surprising result indicates that the reagents which are attacking the hydrocarbon are substantially constant throughout the irradiation. The attack on the hydrocarbon can be written:

$$\frac{d(HC)}{dt} = -\Sigma_i k_i R_i (HC)$$

where R_i is a reagent (e.g. O, O_3, OH, NO_3) which attacks hydrocarbon with a rate constant k_i. This can be rearranged and integrated to give $\log C_o/C_f = 0.434\ \Sigma k_i \int_o^t R_i dt$.

The linearity of the log versus time plot indicates that the last term is linear with time and therefore that either all R_i's are constant or that somehow the changes in the R_i's counteract each other. Previous irradiations did show a slowing down of the rate after prolonged irradiation (24 hours).[7] Before these ambient air experiments were done it seemed possible that the reaction would slow down or even stop after a few hours of irradiation because of consumption of photoinitiators. From these two irradiations relative rates of reaction of various hydrocarbons were derived by calculating $\log_{10} C_o/C_f$ with the results shown in Table 11. For the olefins these relative reactivities are in reasonable agreement with values determined in synthetic mixtures at concentrations two or three orders of magnitude higher and reported several years ago.[8] The equipment and procedure used at that time did not permit evaluation of the rates of the less reactive hydrocarbons.

Table 11

Relative Rates of Disappearance of Hydrocarbons Under Irradiation

	Blacklight		Sunlight		Ref (8)
	log C_o/C_f	Ratio[a]	log C_o/C_f	Ratio[a]	
Ethene	0.217	1.00	0.345	1.00	0.83
Propene	0.818	3.8	1.45	4.2	3.8
1-Butene	0.823	3.8	0.79	2.4	---
i-Butene	0.665	3.1	0.895	2.6	5.2
tr-2-pentene	4.2	19	---	---	(22-18)[b]
n-butane	0.095	0.44	0.090	0.26	
n-hexane	0.132	0.61	0.167	0.48	

[a] Ethene = 1.00 [b] 2-butene and 3-hexene

The relative contributions of olefins and paraffins were expressed in another way by summing the amounts reacted after each time period with the result shown in Figure 37 which was derived from the same experiment as Figure 35. This plot is curved because the olefins react more rapidly and so are depleted earlier in the experiment. After eight hours about 130 ppb of olefin (mostly accounted for by propene and ethene) and 46 ppb of paraffin had reacted. Inclusion of higher molecular weight hydrocarbons would change this picture somewhat, principally by inclusion of the moderately reactive aromatics. According to air monitoring data the original mixture contained 0.14 ppm (140 ppb) of nitric oxide which would, according to present understanding of the photochemical reaction, be converted to nitrogen dioxide in the first stages of the reaction. Laboratory studies suggest that oxidation of one molecule of hydrocarbon is capable of converting about two molecules of nitric oxide.[11] Then about 70 ppb of hydrocarbon would be

required for conversion of the nitric oxide initially present. If we estimate that the total hydrocarbons reacting are twice the amount measured this might require about two hours of irradiation.

Auto Exhaust Irradiation

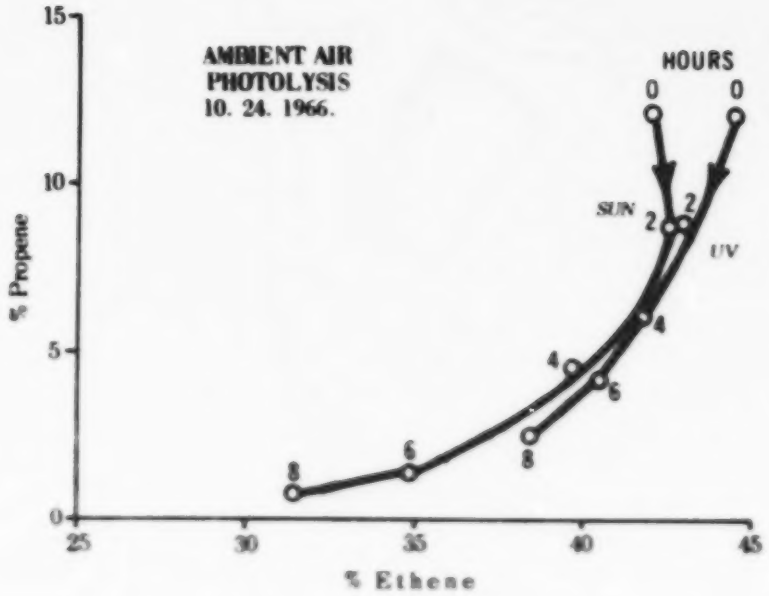
A sample of auto exhaust diluted with purified air was irradiated with ultraviolet to generate the data shown in Figure 38. This sample was obtained with the cooperation of Scott Research Laboratories. A 1963 V-8 Chevrolet using "basin mix" gasoline and running on a chassis dynamometer in the California standard driving cycle was used as a source of exhaust. Exhaust from a single cycle was collected in a plastic bag after thorough warm-up of the engine. A 20 ml portion of exhaust gas was transferred to the 20 L bottle which had previously been flushed with purified air (also obtained from Scott Research Laboratories). This 1000-fold dilution produced a mixture which, except for propane and other light paraffins, closely resembled that obtained from ambient air. The contents of the bag were also analyzed by the nondispersive infrared instruments used for exhaust testing. This showed 305 ppm of hydrocarbon (as n-hexane), 3.5% carbon monoxide, and 8.2% carbon dioxide. This hydrocarbon concentration is below average but not enough to be considered atypical. The rates of disappearance of the individual hydrocarbons in this experiment were approximately the same as in the ambient air experiment. The reason for the curvature of some of the plots is not known.

Extent of Reaction

This type of irradiation data can be compared to ambient air analyses to judge the extent to which reaction has occurred. This is important because it bears directly on the value of various control strategies which call specifically for a reduction of the most reactive hydrocarbons. From laboratory studies of auto exhaust irradiation, it was not possible to tell whether most of the reaction was due to the high reactivity compounds (higher molecular weight olefins) or whether actual ambient air conditions were such that hydrocarbons of medium

and low reactivity could participate. This is related to the time available for reaction; or the effective residence time of pollutants in the atmosphere. Acetylene, ethene and propene form a unique set of compounds for judging the extent of reaction since they are almost exclusively derived from auto exhaust; they are emitted in known ratios to each other (see Table 9), and they differ quite widely in reactivity. Dilution will reduce all three concentrations in proportion, but photochemical reaction will destroy the propene most rapidly, the ethene at a moderate rate and the acetylene very slowly. Extent of reaction could be judged either by the propene/acetylene rat or by the ethene/acetylene ratio. To make use of both ratios the sum of the three hydrocarbons was taken and each olefin expressed as a percentage of the total. These percentages for the batch irradiation of ambient air samples gave Figure 39 when plotted against each ot A similar experiment carried out at the winter solstice (minimum solar radiation) showed similar reactivity for both sunlight and ultraviolet irradiation (Figure 40). It is obvious that smog samples could be plotted on this chart to judge the effective reaction time. But it should be remembered that these were batch experiments, whereas the outside air has continuous addition of pollutants. The other extreme would be a stirred flow reactor at some stated residence time. Since there was no way to determine this on an ambient air sample the expected behavior was calculated from the batch experiments.

With constant intensity of irradiation (UV) the rate of disappearance was nearly first order (see Figure 36). First order rate constants derived from these laboratory data were then used to compute the theoretical change in composition of the mixture in the proportions given above both for a batch reaction in which concentrations decrease exponentially according to the equation $C = C_o \exp(-kt)$ and for a stirred flow reactor in which case the concentrations fall according to $C = C_o(1 + kt)^{-1}$. These two extreme types of reactor give different plots as shown in Figure 41 . The actual atmosphere is probably somewhere between these two.



	Ratio	%	k (hr^{-1})
Acetylene	1.00	47.6	0.0159
Ethene	0.85	40.5	0.1013
Propene	0.25	11.9	0.417

FIGURE 39

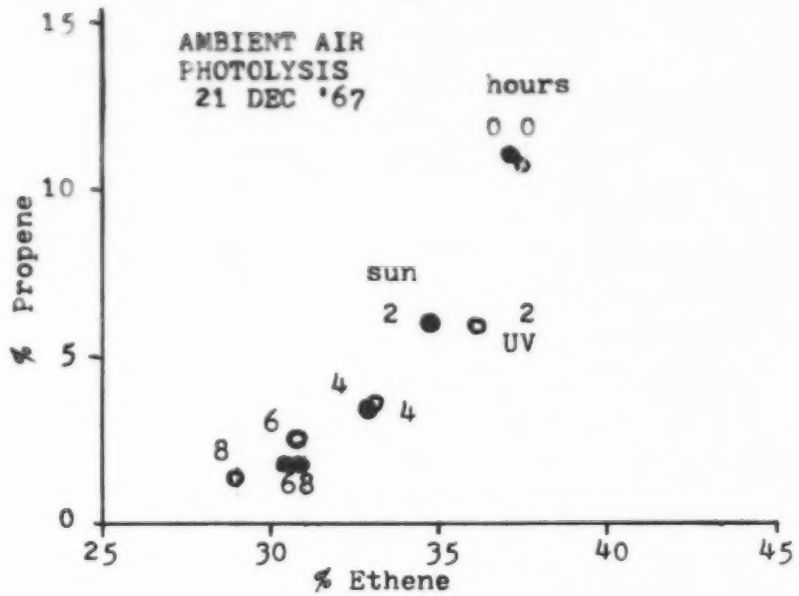
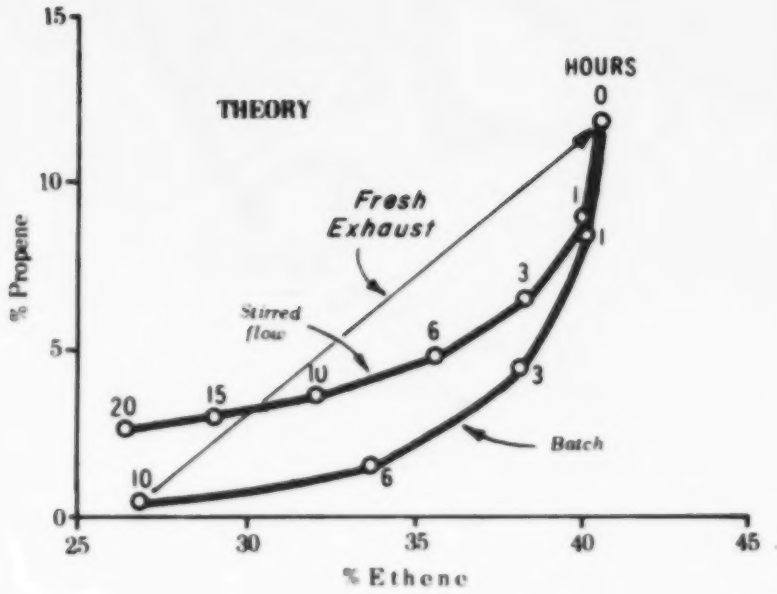


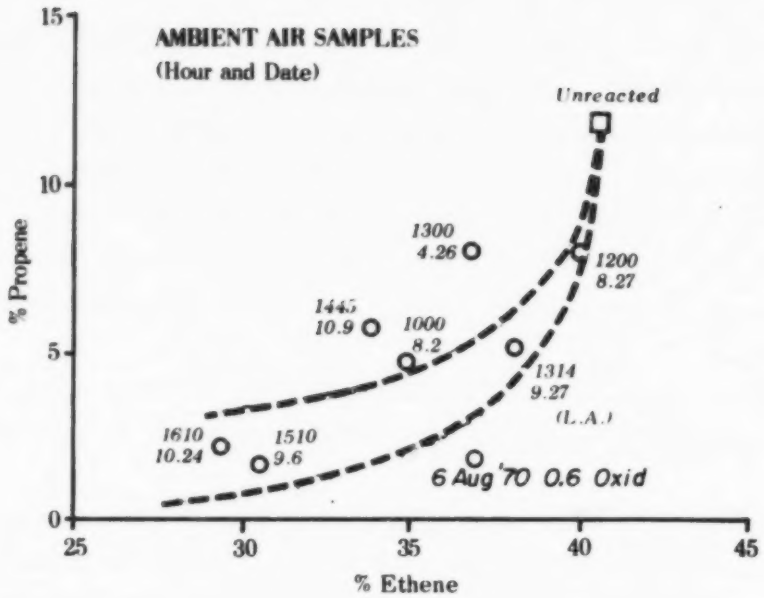
FIGURE 40



AMBIENT AIR PHOTOLYSIS.
(Ethene + Propene + Acetylene = 100 %)

FIGURE 41

If additional exhaust gas is added to a reacted mixture (say 10 hours batch reaction as shown in Figure 41) the composition will be moved along the straight line marked "fresh exhaust." Such addition, of course, also lowers the average irradiation time of the mixture. Since all types of history are possible, atmospheric samples may lie anywhere within the crescent area of Figure 41. In Figure 42 are plotted the observed percentages for a number



EXTENT OF PHOTOLYSIS OF AMBIENT AIR.
(Ethene + Propene + Acetylene = 100%)

FIGURE 42

of smog samples. Most of the data lie in or near this crescent. In fact, the two best sets of samples (9/6/68 and 10/24/68) fall near each other and between the curves for stirred flow and batch reaction near the point corresponding to eight hours of irradiation. The Pacific Standard

Time at which each group of samples was taken is given along with the date. All but one set of samples were taken in Riverside. Although there is considerable scatter the points do lie in the general area of the stirred flow and batch reactor plots of Figure 41 and the samples taken later in the day show the most reaction.

The data for the 0.6 oxidant day of August 6, 1970 is slightly below the curve for batch reaction. It is tempting to interpret this as meaning this air was reacted for several hours in isolation from fresh exhaust. Perhaps this could happen if a parcel of air irradiated aloft were brought down to the surface. Recent research has suggested that high oxidant levels are sometimes formed aloft. In such circumstances, a parcel of polluted air might undergo reaction and then be brought down to the surface.

The samples taken on 10/24/68 showed the highest degree of reaction, along with some of the highest concentrations of any set of samples. These were taken in late afternoon just after a very sharp pollution front passed Riverside. By comparing this afternoon's analysis with an unreacted morning sample it was possible to make a crude estimate of the amounts of the various hydrocarbons which would have been present if no reaction had occurred. The following assumptions were needed:

1) Reaction equivalent to 10 hours in the ultraviolet bottle reactor had occurred. This was based on the plots shown in Figures 39 and 42.

2) A set of first order rate constants k_i-(hr^{-1}) were derived from the bottle photolysis. These were used in the first order stirred flow rate expression $C_o = C(1 + kt)$ with $t = 10$ hours to calculate the amounts of acetylene and other hydrocarbons of low reactivity present before reactions. Use of batch kinetics would make little difference here.

3) The amounts of ethene and propene were estimated from the acetylene concentration and the ratios of these hydrocarbons in unreacted exhaust.

4) The C_4 and C_5 olefins before reaction were assumed to be equal to the amounts found in the unreacted morning sample because the amounts

of C_5-C_6 paraffins were similar. Both groups are probably derived primarily from gasoline.

5) A previously published analysis of "basin-mix" fuel was used along with an estimated gasoline composition of 11% olefin, 35% aromatic and 54% saturate. These were used to estimate the amounts of higher hydrocarbons in the three classes which went unmeasured. The higher saturates were assumed to have been comparable in reactivity to the C_5-C_6 paraffins and the higher olefins assumed to be 90% reacted. Reactivities for the aromatics were estimated from Stephens and Scott[8] (generally between ethene and propene except benzene, toluene and ethylbenzene, all = 0). These latter are extrapolations on top of estimates so they must be quite crude.

These results are summarized in Tables 12 and 13 . The total amount reacted is estimated to be just under 200 ppb which is less than one-third of the amount initially present. If auto exhaust contains 250 ppm of acetylene and 1500 ppm of nitric oxide, we might judge that before reaction this sample would have had 300 ppb of nitric oxide. It is somewhat surprising that reaction of 200 ppb of hydrocarbon could accomplish the conversion of 300 ppb of nitric oxide to nitrogen dioxide and the further reaction of this to PAN and other products. PAN and nitrogen dioxide only accounted for about one-third of this estimated 300 ppb of nitric oxide. Some of the samples shown in Figure 42 were much less reacted than the sample of 10/24/68. Even so they had the symptoms of air pollution even for these very small degrees of reaction. It would be interesting to try to determine, using this kind of atmospheric data, the degree of reaction required to reach some critical point of reaction such as the first appearance of ozone. One attempt was made to determine the first appearance of PAN during laboratory irradiation of ambient air, but no lag was apparent. The PAN began to form as soon as irradiation was started; it may be that this ambient air sample was not completely unreacted at the beginning.

Table 12 Estimate of amounts reacted in an ambient air sample compared to an unreacted sample.

	Reacted Sample (ppb) 1610 PST 10/24/68		Unreacted Sample (ppb) 0730 PST 9/24/68
	Present	Reacted (Δ)	Present
Methane	2530	0	2355
Ethane	72.2	0.6	53.6
Propane	49.9	2.6	18.8
[C]Acetylene	42.0	6.3	77.0
Ethene	17.9	23.1	65.6
Propene	1.27	10.7	19.2
Methyl Acetylene	1.2	0.3	2.6
1,3-Butadiene	0.29	1.5	3.6
[O]1-Butene	0.26	2.3	2.6
Isobutene	2.0	3.2	5.2
Trans-2-Butene	<0.2	1.4	1.4
Cis-2-Butene	<0.2	1.4	1.4
2-Methyl Butene-1	0.35	2.1	2.4
Cyclo Pentene[a]	0.8	3.2	4.4
Trans-2-Pentene	<0.2	2.4	2.4
2-Methyl Butene-2	<0.2	2.6	2.6
[P]Isobutane	19.7	3.0	8.0
N-butane	62.0	16.3	27.6
Isopentane	41.2	12.8	39.2
N-Pentane[b]	21.4	7.9	22.4
Cyclo Pentane	2.4	0.6	3.2
2,2-Dimethyl Butane[c]	0.86	0.3	1.6
2,3-Dimethyl Butane	1.9		3.8
2-Methyl Pentane[d]	9.6	4.4	12.4
3-Methyl Pentane	6.1	3.9	8.4
N-hexane	8.3	3.5	9.0

Includes: [a] 2-Methyl Butadiene-1,3; [b] 3-Methyl Butene-1; [c] 1-Pentene; [d] Cis-2-Pentene.
C, O, P—See Table V

Table 13 Riverside ambient air (ppb) on roof of health-finance building. 1610 PST 10/24/68 (In ppb by volume except where noted.)

Compound	Present	+	Reacted[a]	=	Initial[a]
C_1 - C_2 Paraffins (meas.)	2652		3.2		2655
Non-fuel unsaturated[C] (meas.)	62.7		41.9		104.6
C_4 - C_5 Olefins[O] (meas.)	3.4		18.6		22.0
C_4 - C_5 Paraffins[P] (meas.)	173.5		52.7		226.2
Higher olefins (est.)	2.2		19.6		21.8
Higher saturates (est.)	42		21.0		63.0
Aromatics (est.)	67		40.9		107.9
Total (less CH_4)	473		198		671
Total (ppbC, incl CH_4, GLC)	4800				
Total (ppbC, non GLC)	6000				
Acetylene	42.0				48.3
Carbon monoxide	5000				
Oxidant	400				
Nitrogen oxides	60				300
PAN	34				

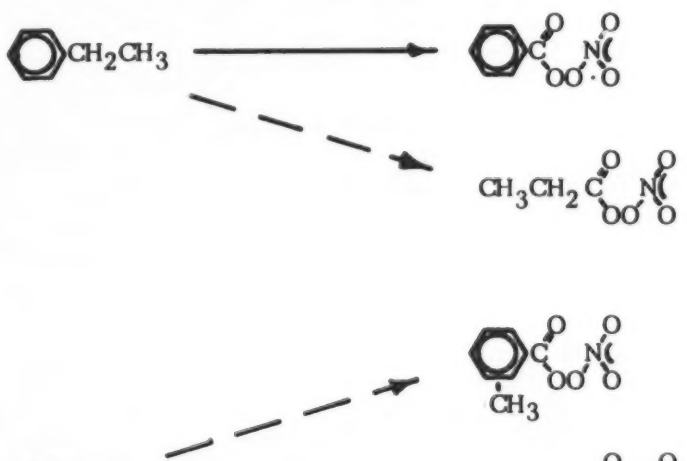
[a] estimated
C, O, P—See Table IV

MODES OF REACTION

This comparison of smog hydrocarbon distribution with irradiated samples indicated that hydrocarbons of all classes participated in the reaction. Even the aromatics (except benzene) react substantially in the time available. During the course of this program Heuss and Glasson at General Motors discovered that benzilic hydrocarbons[12]

could be oxidized under atmospheric conditions to peroxybenzoyl nitrate, an extremely potent eye irritant. This was surprising not only because of the eye irritation but also because it indicated that side chain oxidation occurred. In contrast, xylenes and mesitylene produced PAN, clearly showing that ring rupture occured.

OXIDATION OF MONO AND DI ALKYL BENZENES



This striking difference in products clearly indicates a difference in active species attacking the hydrocarbon. The active species most suggested for this role are atomic oxygen, ozone and hydroxyl radicals. Ozone reacts rapidly with olefins but its reaction with aromatics is too slow to be considered. Atomic oxygen is known to attack aromatic hydrocarbons in the ring so it might be suspected that side chain oxidation is initiated by hydroxyl radical. Another possibility is the NO_3 radical which is formed by the reaction of ozone with NO_2. All these active species are present in steady state, and the probable reactions and steady state equations are as follows:

REACTIVE SPECIES

O ATOMS

$$NO_2 \xrightarrow{\emptyset k_a} NO + O$$

$$O + O_2 + M \xrightarrow{k_3} O_3 + M$$

$$(O) = \frac{\emptyset k_a (NO_2)}{k_3 (O_2)(M)}$$

O_3

$$O_3 + NO \xrightarrow{k_4} NO_2 + O_2$$

$$(O_3) = \frac{\emptyset k_a (NO_2)}{k_4 (NO)}$$

$NO_3 \cdot$

$$NO_2 + O_3 \xrightarrow{k_5} NO_3 + O_2$$

$$NO_3 + NO_2 \xrightarrow{k_6} N_2O_5$$

$$(NO_3) = \frac{k_5 (O_3)}{k_6}$$

$OH \cdot$

It is noteworthy that the NO_3 steady state concentration is directly proportional to the ozone concentration and independent of the nitrogen

dioxide concentration. Calculations based on published rate constants yield an NO_3 concentration of 2×10^{-5} (O_3).

MECHANISM

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad k_2$$

$$NO_3 + NO \rightarrow 2NO_2 \qquad k_9$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \qquad k_{10a}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad \text{fast}$$

$$(NO_3)\ \text{Steady State} = \frac{k_2(NO_2)(O_3)}{k_9(NO) + k_{10a}(NO_2)}$$

$$(NO)/(NO_2) \rightarrow 0$$

$$(NO_3) = 2 \times 10^{-5}\ (O_3)$$

There are a few hints in the literature that NO_3 might be able to abstract atomic hydrogen from organic molecules. Principal evidence[13] is the ability of N_2O_5 to react with aldehydes in air in the dark to produce PAN. Another reaction was attributed to NO_3 by Wilson[14]

$$NO_2 + O_3 + SO_2 \rightarrow \text{aerosol}$$

If various species were attacking different hydrocarbons at different rates, the rates of disappearance should vary during the course of the reaction. This did not seem to be true in the ambient air irradiations. A test with three selected hydrocarbons (one paraffin, one olefin and one aromatic) in the 20 liter bottle showed no variations in the rate of consumption of all three hydrocarbons after five hours of irradiation. (See Figure 43)

Since this was an uninformative result, it was decided to try to maximize the opportunity for reaction of NO_3. This was done in two ways:

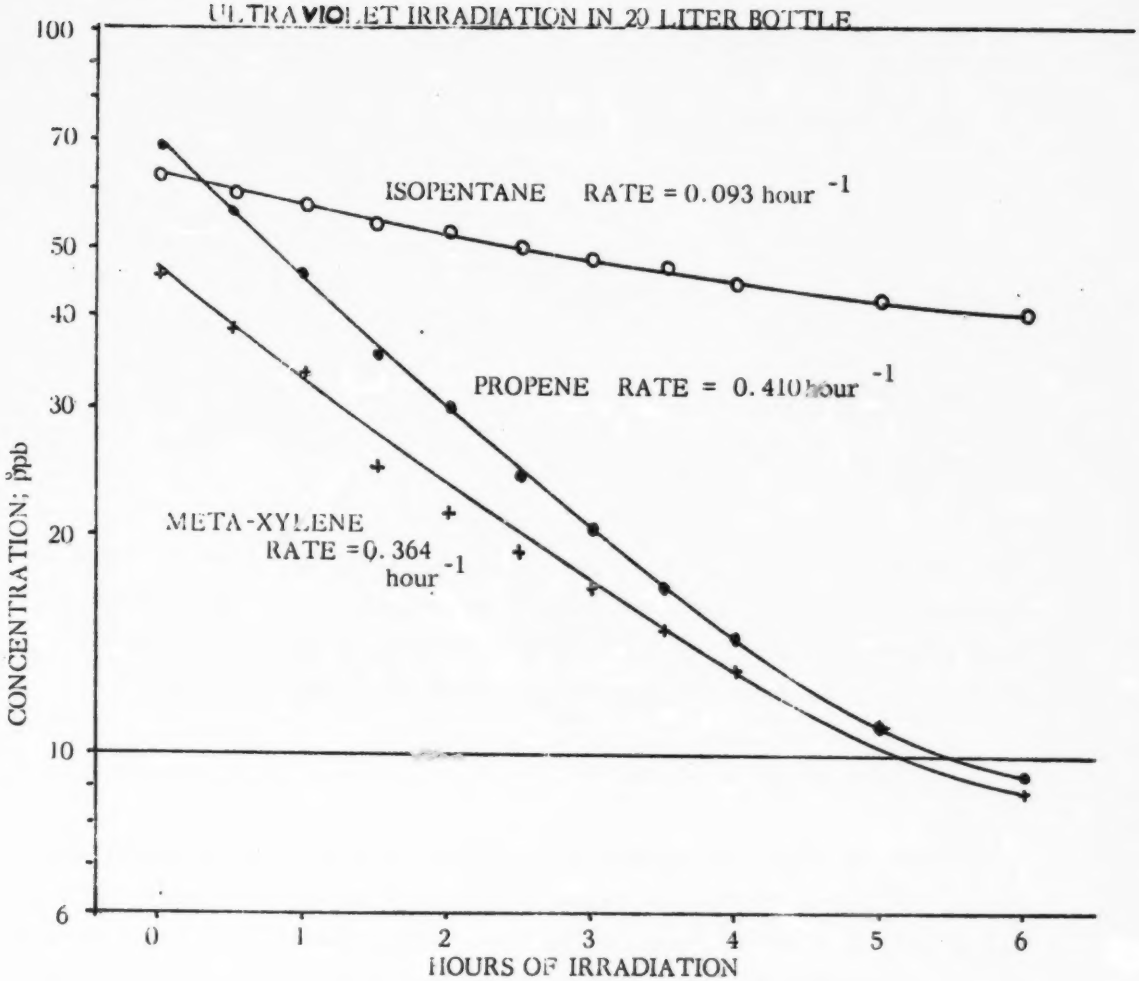

ULTRAVIOLET IRRADIATION IN 20 LITER BOTTLE
100
70
50
40
30
20
10
6
CONCENTRATION; ppb
ISOPENTANE RATE = 0.093 hour -1
PROPENE RATE = 0.410 hour -1
META-XYLENE
RATE = 0.364
hour -1
0
1
2
3
4
5
6
HOURS OF IRRADIATION

FIGURE 43

1) some high concentration experiments were done in the long-path infrared cell, and 2) the 50 liter stirred flow reactor was used with mixtures of NO_2, O_3 and selected hydrocarbons in the dark. In the infrared cell concentrations of 500-800 ppm of an aromatic hydrocarbon were mixed with about 1000 ppm of nitric oxide and ozone (to generate NO_3 and N_2O_5). Even at these high concentrations the reaction was not fast. Principal effort was directed toward detection and measurement of peroxybenzoyl nitrate (PBzN). This compound has a distinctive band at 987 cm^{-1} which has been used to identify PBzN produced from benzaldehyde. Electron capture chromatography was also used to identify the PBzN and PAN estimated from the infrared spectra are given in Table 14.

TABLE 14

	HC ppm	PBzN	PAN
Toluene	590	0.91	-
Ethyl benzene	737	0.56	-
n-Butyl benzene	581	3.52	-
1,3,5-trimethyl benzene	633	-	8.4

This positive result showed that aromatic hydrocarbons can produce PBzN in a dark reaction, but the very slow yields indicate that this is of little importance.

Stirred flow experiments were then carried out at 3000 fold lower concentrations in the flow photoreactor. Since longer chain benzilic hydrocarbons were more reactive than toluene, n-propyl benzene was included in this series. The results indicate that at this concentration level little reaction occurs even in residence times of several hours.

The hydrocarbon mixture, the NO_2, and O_3 were dispensed from separate LPO tanks, using hi-pure N_2 as the diluent in all cases. LPO concentrations were sought such that convenient dispensing rates through the rotometer flow panel would admix with the carbon filtered air in the mixing manifold and pass finally into the 50 liter reaction bottle producing approximately:

in the first experiment -

HC	-	200 ppb
NO_2	-	0.2 ppm
O_3	-	0.5 ppm

and in the remaining experiments -

HC	-	200 ppm
NO_2	-	1.0 ppm
O_3	-	2.5 ppm

In all experiments acetylene was added to the HC LPO tank to assist in monitoring dispensing regularity and mixing. In the last experiment trans butene-2 was added to demonstrate the capability of obtaining a dark reaction at the concentrations used in the experiments with the equipment as it was presently devised.

HC measurements were made by the standard concentration technique, from samples taken at the 50 bottle inlet or exhaust ports, and subsequently analyzed on the appropriate FID gas chromatograph.

NO_2 concentrations were determined colormetrically using Saltzman's reagent.

O_3 concentrations were determined using the Mast ozone meter.

TABLE 15. Reactivity of Aromatic Hydrocarbons in the Flow Photoreactor

		ppb inlet				ppb exhaust				ppm inlet		ppm exhaust	
Page No.	Cond.	$C_2=$	$C_1\phi$	$NC_3\phi$	$T_2C_4=$	$C_2\equiv$	$C_1\phi$	$NC_3\phi$	$T_2C_4=$	O_3	NO_2	O_3	NO_2
46	1 hr Dark	239	119	-	-	232	108	-	-	.42	.13	.32	.09
48	1 hr Dark	-	-	-	-	249	123	-	-	off scale	.68	.11	.68
52	2 hrs Dark	232	210	-	-	228	205	-	-	off scale	.99	.58	.18

TABLE (continued)

Page No.	Cond.	ppb inlet $C_2^=$	$C_1\emptyset$	$NC_3\emptyset$	$T_2C_4^=$	ppb exhaust $C_2\equiv$	$C_1\emptyset$	$NC_3\emptyset$	$T_2C_4^=$	ppm inlet O_3	NO_2	ppm exhaust O_3	NO_2
55	1 hr	230	280	-	-	232	284	-	-	off scale	1.07	-	-
* 55	2 hrs Dark	227	284	-	-	230	279	-	-	measurement taken 12 hrs after end of expt			
55	4 hrs Dark	232	270	-	-	236	266	-	-				
57	1 hr U-V light	243	317	-	-	233	294	-	-	same LPO tank as above; no O_3 or NO_2 measurements taken			
57	2 hrs U-V light	249	302	-	-	250	288	-	-				
* 58	4 hrs U-V light	243	284	-	-	232	269	-	-				
58	static U-V light	[228	218	(T-0)]	-	(168	56	(T=24 hrs)]					
61	1 hr Dark	233	-	218	-	230	-	230	-	-	-	.37	.62
61	2 hrs Dark	246	-	204	-	243	-	216					
62	4 hr Dark	224	-	189	-	227	-	179					
62	4 hrs U-V light	230	-	163	-	224	-	163					
62	static U-V light	-	-	-	-	(192	-	69	(T=15 hrs)]				
66	1 hr Dark	201	-	179	122	200	-	192	40	off scale	1.4	.23	1.3

*Continuous experiments

Table 16 summarizes the data for all of the experiments. The percent reactions of the aromatic hydrocarbons used are as follows:

	DARK			LIGHT			
	1 hr	2 hrs	4 hrs	1 hr	2 hrs	4 hrs	static
$C_1Ø$	2%	2%	2%	7%	5%	5%	75%
$NC_3Ø$	neg	neg	5%	-	-	0%	58%*
$T_2C_4=$	67%	-	-	-	-	-	-

*Based upon a 15 hour static reaction; presuming linearity, in 24 hours (as was the time with $C_1Ø$), this $NC_3Ø$ reaction would have gone to 93%.

The 67% dark reaction (residence time = 1 hr) of $T_2C_4=$ demonstrates the capability of the hardware as devised and the suitability of the concentrations of the other reactants. The static reactions demonstrate a similar capability in the presence of U-V light. Although the dark reaction has been reported at considerably higher concentrations, the present series of experiments suggest that at these lower concentrations the reaction occurs at a rate too low for detection by the instrumentation and procedures utilized.

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